



Semiconducting properties of p- and n-type organic nanofiber/poly (methyl methacrylate) composite films for film rectifier



Morito Yagi, Noriyuki Ito, Masahiro Kawasaki, Takeshi Shimomura*

Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

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ABSTRACT

We investigated the field-effect mobility of regioregular poly(3-hexylthiophene) (P3HT) and *N,N'*-ditridecyl-3,4,9,10-perylenetetracarboxyl diimide (PTCDI-C13) nanofibers composited in poly(methyl methacrylate) (PMMA) with varying P3HT/PMMA or PTCDI-C13/PMMA ratio, solvent species, and doping concentration by fabricating the field effect transistor (FET) of these composite films. Both composite films functioned as a p- or n-type semiconducting layer of FET, and the apparent field-effect mobility gradually increased with increasing P3HT or PTCDI-C13 ratio, and was estimated to be about $4.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (P3HT nanofiber/PMMA composite, P3HT weight ratio = 10%) and $2.0 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (PTCDI-C13 nanofiber/PMMA composite, PTCDI-C13 weight ratio = 20%). In addition, a pn junction between P3HT nanofiber/PMMA and PTCDI-C13 nanofiber/PMMA composite films was fabricated to examine the rectifying effect. The rectifying effect was obtained and an appropriate diode region was observed in the forward current with the ideal factor *n* of 2.30. The rectifying effect can be derived by a simple fabrication method, i.e., simply pasting n- and p-type flexible films together, which gives us a novel methodology for fabricating flexible semiconducting devices.

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1. Introduction

Conducting polymer nanofibers have attracted increasing interest owing to their unique shapes and electric properties for various applications such as in molecular wires, organic transistors, and sensors [1–3]. In particular, nanofibers of regioregular poly(3-alkylthiophene) (P3AT) with a whisker structure crystallized from supercooled solutions in adequate solvents have a fine structure with a width and a length of 15 nm and several μm , respectively [4]. These nanofibers function as the p-type active layer of a field-effect transistor (FET) with a considerably high field-effect mobility similar to those of P3ATs [5], and the transfer and output characteristics of this FET using nanofibers have been extensively investigated in the thin-film state [6–12], entangled networks [13,14], and isolated single fibers [5,10,15–17].

Recently, Qiu et al. have reported that P3HT can be recrystallized into the nanofiber form in conventional noncrystalline polymers such as poly(methyl methacrylate) (PMMA) and polystyrene (PS) to form nanofiber composite films [18–20]. These nanofiber composite films exhibit semiconducting properties and could be fabricated into a flexible FET by simply attaching

electrodes. By Kelvin probe force microscopy (KFM) we have also observed that an effective nanofiber network can be percolated over these films [21]. In addition, these composite films could be doped and represented as potential flexible films with considerable mechanical strength and both high transparency (due to the transparent matrix) and high conductivity (due to the well-developed P3HT nanofiber network) with high environmental stability [22]. From these results, it would be expected that this P3AT nanofiber composite film can be regarded as a flexible semiconducting substrate substituting for the nonflexible silicon substrate.

In addition, n-type nanofibers made from some organic compounds, such as poly(benzobisimidazobenzophenanthroline) (polyBBL) [23] and perylenetetracarboxyl diimide (PTCDI) derivatives [24–26], have been reported. These nanofibers also worked as the n-type active layer of the FET, but their field-effect mobilities (10^{-5} – $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are smaller by some order of magnitude than those of p-type nanofibers. In particular, PTCDI derivatives were reported to form spontaneously fine nanofibers of 80–300 nm widths at the interface between chloroform and MeOH, and the mobility of a single PTCDI nanofiber was also measured by conductive atomic force microscopy (C-AFM) [26].

These n-type nanofibers can be also embedded in conventional noncrystalline polymers and form composite films. Thus, in this

* Corresponding author.

E-mail address: simo@cc.tuat.ac.jp (T. Shimomura).

study, we used the nanofiber made from *N,N'*-ditridecyl-3,4,9,10-perylenetetracarboxyl diimide (PTCDI-C13) and embedded in PMMA to form PTCDI-C13 nanofiber composite film. Furthermore, we determined the field-effect mobility of regioregular poly(3-hexylthiophene) (P3HT) and PTCDI-C13 nanofibers composited in PMMA with varying P3HT/PMMA or PTCDI-C13/PMMA ratio, species of solvent, and doping concentration by fabricating the FET. In addition, a pn junction between P3HT nanofiber/PMMA and PTCDI-C13 nanofiber/PMMA composite films was fabricated to examine the rectifying effect. The rectifying effect can be derived by a simple fabrication method, i.e., simply pasting n- and p-type flexible films together, which gives us a novel methodology for fabricating flexible semiconducting devices.

2. Experimental

2.1. Preparation of P3HT nanofiber/PMMA composite

Regioregular poly(3-hexylthiophene) (P3HT) (M_w 44,000) was purchased from Sigma–Aldrich Co., Inc. (St. Louis, MO, USA), and used as a p-type nanofiber without further purification. We chose poly(methyl methacrylate) (PMMA) to form the matrix of the composite film, as reported previously [18–20]. PMMA (M_w 120,000) was also purchased from Sigma–Aldrich and used without further purification. P3HT nanofiber composite films were prepared by the following simple procedure [21,22]. P3HT and PMMA powders were added into a solvent mixture composed of chloroform (as a good solvent of P3HT) and anisole (as a poor solvent of P3HT), such that the concentration of the polymer blend was 1 wt%, with stirring at 60 °C. P3HT/PMMA solutions were prepared at P3HT weight ratios of 50, 10, 5, and 3 wt%, in a fixed 50:50 (v/v) solvent mixture of chloroform/anisole. As previously reported, the film with the P3HT weight ratio less than 1 wt% tended not to show significant conductivity over the bulk film [22]. In addition, composite films with the P3HT weight ratio of 5 wt% were prepared in chloroform/anisole mixed solvents at ratios of 70:30, 30:70, and 10:90 (v/v). Each solution was cooled gradually to 20 °C at a rate of 25 °C/h without stirring. Then, the solution changed from a transparent yellow one to a turbid reddish-brown suspension, which became evident after the solution sat undisturbed, in air ambient, for one week.

2.2. Preparation of PTCDI-C13 nanofiber/PMMA composite

N,N'-Ditridecyl-3,4,9,10-perylenetetracarboxyl diimide (PTCDI-C13) was purchased from Sigma–Aldrich Co., Inc. (St. Louis, MO, USA), and used as an n-type nanofiber without further purification. PMMA (M_w 120,000), purchased from Sigma–Aldrich Co., Inc., was used as a matrix in the same way as in the P3HT nanofiber composite. A PTCDI-C13 nanofiber/PMMA composite was prepared as follows [25]. PTCDI-C13 powder was dissolved in chloroform (0.50 mg/mL, 6 mL), and MeOH (6 mL) was poured gently to the solution. Then, the solution was separated into the transparent upper layer (MeOH) and the bottom layer (PTCDI-C13 in chloroform) with yellow fluorescence immediately after adding MeOH. The solution was gently mixed with a pipette to disturb the layers; then, reddish nanofibers were crystallized and precipitated. For a dopant, [4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)phenyl]dimethylamine (N-DMBI), purchased from Sigma–Aldrich Co., Inc., dissolved in chlorobenzene was added to the suspension of precipitated nanofibers, in which the molar ratio of N-DMBI to PTCDI-C13 was 10, 3, 1, or 0.5%. Finally, PMMA was added to the dispersion, in which the weight ratios of PTCDI-C13 were adjusted to 30, 20, 15, and 10 wt%.

2.3. Characterization of P3HT/PMMA and PTCDI-C13/PMMA composite films

Pt (P3HT/PMMA) or Au (PTCDI-C13/PMMA) electrodes with a length of 0.6 mm and a gap space of 40 μ m were fabricated with a bottom-contact configuration by sputter deposition using a shadow mask on a piece of doped Si wafer with a 255 nm thermally grown SiO₂ layer on top (SiO₂/Si) purchased from KST World Corp. (Fukui, Japan). Thin films of P3HT/PMMA or PTCDI-C13/PMMA composites were prepared by the spin casting of P3HT/PMMA or PTCDI-C13/PMMA suspensions at 3000 rpm for 30 s on the SiO₂/Si substrate with Pt electrodes and the residual solvent on the substrate was removed by vacuum drying.

The thin films of P3HT/PMMA or PTCDI-C13/PMMA composite were observed in air ambient with a Nanoscope scanning probe microscope (SPM; Hitachi High-Tech Science Corp., Tokyo, Japan) in the scanning force microscope (SFM) mode. A Si cantilever (OMCL-AC160TS-C3, Olympus Corp., Tokyo, Japan; spring constant, 26 N/m; resonant frequency, ca. 300 kHz) was used in the intermittent-contact mode. FET measurement was carried out by a two-probe method in vacuum below 10⁻⁵ Torr at room temperature using a system combining the cryostat CRT-006, the Keithley model 236 source measure unit (SMU) (Keithley Instruments, Inc., Cleveland, OH, USA) for measuring the source-drain characteristics, and a Keithley 2400 digital source meter (Keithley Instruments, Inc.) for applying the gate field.

2.4. Characterization of pn junction between P3HT nanofiber/PMMA and PTCDI-C13 nanofiber/PMMA composite films

The preparation of a pn junction between P3HT nanofiber/PMMA and PTCDI-C13 nanofiber/PMMA composite films is shown in Fig. 1. Au electrodes with a length of 0.6 mm and a gap space of 40 μ m were fabricated with a bottom-contact configuration by sputter deposition using a shadow mask on a piece of Si wafer with a 255 nm thermally grown SiO₂ layer on top (SiO₂/Si). One of the electrodes was masked using a masking tape, and a thin film of P3HT/PMMA composite was fabricated by the spin casting of a P3HT/PMMA suspension at 1500 rpm for 30 s. After peeling off the masking tape and drying the substrate under vacuum, a PTCDI-C13/PMMA suspension was drop casted on P3HT nanofiber/PMMA composite masked using masking tape, and finally, the residual solvent on the substrate was removed by vacuum drying. The *I*-*V* measurement between electrodes was measured using the Keithley model 236 source measure unit to investigate the rectifying effect.

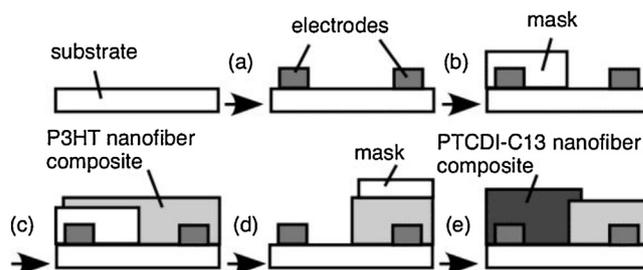


Fig. 1. Preparation of pn junction between P3HT nanofiber/PMMA and PTCDI-C13 nanofiber/PMMA composite films: (a) sputtered deposition of electrodes, (b) masking one electrode, (c) spin casting of P3HT nanofiber/PMMA composite film, (d) peeling off the mask and masking the other side, and (e) spin casting of PTCDI-C13 nanofiber/PMMA composite film.

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