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Self-assembly of ordered poly(3-hexylthiophene) nanowires for organic field-effect transistor applications

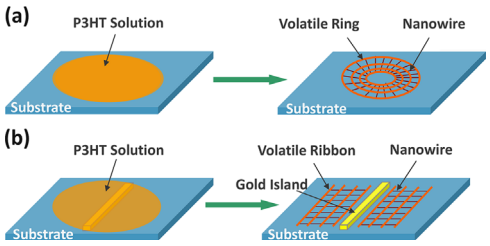
Zongpeng Zhu [a,b], Jun Wang [b], Bin Wei [b,*]

[a] School of Materials Science and Engineering, Shanghai University, Shanghai 200072, People's Republic of China
[b] Key Laboratory of Advanced Display and System Application, Ministry of Education, Shanghai University, Shanghai 200072, People's Republic of China

HIGHLIGHTS

- A gold island structure is proposed to prepare ordered P3HT nanowires.
- Dichlorobenzene is an ideal solvent to grow ordered P3HT nanowires.
- The length and width of nanowires are measured to be 20–30 μm and 50 nm, respectively.
- We successfully fabricate OFETs based on P3HT ordered nanowires.
- The mobility and threshold voltage are 0.06 $cm^2/V\,s$ and −13 V, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

A gold island structure is proposed to prepare ordered P3HT nanowires. The optical photographs of P3HT nanostructures self-assembly from different solvents show that dichlorobenzene is an ideal solvent to grow ordered P3HT nanowires. From optical and TEM graphs, the length and width of nanowires are measured to be 20–30 μm and 50 nm, respectively. Finally, we successfully fabricate organic field-effect transistors (OFETs) based on P3HT ordered nanowires with uniform density by introducing this method. The mobility and threshold voltage are 0.06 $cm^2/V\,s$ and −13 V, respectively. Our study may provide a thought in developing and optimizing organic electronic devices.

1. Introduction

In recent years, organic electronics have drawn considerable attention because of the advantages of organic semiconductors, such as low cost, flexibility, large-area fabrication and "bottom-up" assembly [1,2]. In particular, one-dimensional (1D) structures (e.g. nanotubes, nanoribbons, nanofibers and nanowires) are regarded as the most promising candidates for organic electronics and nanoelectronics [3–6]. Amongst the aforementioned nanostructures, organic nanowires self-assembled from conjugated polymers show bright prospect for the applications in organic field-effect transistors (OFETs) [7,8]. As one of the most extensively studied conjugated polymers, poly(3-hexylthiophene) (P3HT) offers relatively high carrier mobility (0.01–0.1 $cm^2/V\,s$) and solution processability [9,10]. However, the carrier mobility of P3HT suffers from the impacts of its regioregularity, molecular weight, solvent properties and crystallization [11–14]. Meanwhile, P3HT crystallization derives from the anisotropic π–π interactions between planar molecular backbones and weak van der Waals interactions between their alkyl side groups [15]. Nevertheless, frequent conjugation breaks and weak π-orbital overlaps in the amorphous phase decrease the charge carrier mobility [16]. Fortunately, the problem will be solved with the realization of ordered nanowires structure.

Although it is very fascinating to fabricate OFETs used ordered nanowires as the active layers, the controlling of location and orientation of nanowires remains challenging for the device

* Corresponding author. Tel.: +86 21 56331431; fax: +86 21 56331977.
E-mail address: bwei@shu.edu.cn (B. Wei).

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applications. Therefore, the correlative studies are still rare. Haiqing Liu et al. [17] fabricated single P3HT nanofiber field-effect transistor via electrospunning with a hole field-effect mobility of 0.03 cm^2/V s. Yuzhan Wang et al. [18] successfully demonstrated the fabrication of highly ordered and large-scale P3HT:PCBM nanowires via a slow-drying method. B.K. Sarker et al. [19] directly grew P3HT crystalline nanowires on aligned array single walled carbon nanotubes (SWNT) to achieve the ordered nanowires. Then, they fabricated the OFETs with prepared nanowires. To date, three main methods are popularly used to fabricate P3HT nanowires: slow solvent evaporation [20,21], recrystallization [22], and blend solvent deposition [23]. For these methods, slow solvent evaporation is the most effective to grow nanowires at low cost. In this paper, we propose a solvent evaporation strategy with a "gold island structure" to prepare ordered P3HT nanowires for OFETs. We first investigated the influence of different solvents on the aggregation of P3HT with optical graphs. Optical and TEM pictures showed the ordered nanowires self-assembly from the "gold island structure". Then the electronic characteristics of OFETs with ordered P3HT nanowires were carried out. All of the results will be discussed in the following parts.

2. Experimental part

2.1. Materials

P3HT (regioregular ratio 99.995%, average M_n 15,000–45,000), anisole, toluene, chloroform and dichlorobenzene(DCB) were purchased from Sigma-Aldrich Co. and used as received, while other chemical solvents of analytical reagent grade were used without further purification. Fig. 1(a) shows the chemical structure of P3HT polymer.

2.2. Sample preparation

First, the different solvents of anisole, toluene, chloroform and dichlorobenzene were prepared. Then P3HT was added to the solvents and heated at 70 °C until it was fully dissolved (orange solution). All samples were made at the same concentration of P3HT (0.2 mg/ml) unless otherwise stated.

2.3. Fabrication of OFETs with ordered P3HT nanowires

A schematic diagram of bottom-gate and bottom-contact OFET is illustrated in Fig. 1(b). Heavily doped n-type silicon wafers (0.01–0.15 Ω cm) with 300 nm thick SiO_2 acted as the substrate and gate electrode. First, the substrates were ultrasonically cleaned with acetone and ethanol for 15 min. Then they were rinsed with deionized water and baked at 120 °C for 10 min. Gold electrodes were deposited and patterned through a shadow mask to define source–drain electrodes with a thickness of 20 nm that defined the device channel width of 300 μm and length of 20 μm. Meanwhile, a 100 nm thick gold island was then deposited on the middle of silicon wafer with the width of 2 mm and length of 2 cm. The gold island structure did not affect gold electrodes for the devices. Finally, the prepared P3HT samples were dropped onto the cleaned substrates and then evaporated for 2 days. Besides, P3HT thin-film field-effect transistor (control device) was also fabricated with the prepared samples by spin coating.

2.4. Characterization

Optical graphs were observed by Leica DM2500M. SEM images were acquired by using a Hitachi S-4800 Scanning Electron Microscope. All electrical measurements were performed using an Agilent 4155C semiconductor parameter analyzer at room temperature in ambient air.

3. Results and discussion

3.1. Influence of different solvents on the aggregation of P3HT

In order to understand the influence of different solvents on the aggregation of P3HT, four groups of experiments were carried out. Fig. 2 shows the optical microscopy images of P3HT nanostructures self-assembly from different solvents ((a) toluene, (b) chloroform, (c) anisole, and (d) dichlorobenzene). From all of the images, it is obvious that volatile rings appear on all these wafers. Interestingly, we observe that ordered nanowires exist between two adjacent rings from Fig. 1(d). Meanwhile, it is worth mentioning that the aggregation of P3HT between two adjacent rings from anisole solvent may be nanowire networks (Fig. 2(c)) [24]. However, no counterparts appear in other solvents (Fig. 2(a) and (b)). Dichlorobenzene is a good solvent and possesses the highest boiling point among the four solvents (180 °C for DCB, 154 °C for anisole, 111 °C for toluene and 61 °C for chloroform). As the evaporation rates were correlated with the boiling points of the solvents [25], dichlorobenzene evaporated more slowly than other solvents which allowed sufficient time for the self-assembly of the ordered nanowires. Thus, we choose dichlorobenzene as one of the ideal solvents to grow ordered nanowires.

3.2. Aggregation of P3HT on the silicon wafer with a gold island

Ordered nanowires between two adjacent rings could be prepared based on the above method. A schematic growth process is illustrated in Fig. 3(a). Notably, there exists a density gradient of ordered nanowires between two adjacent rings. As close to the center, more nanowires appeared along with rings. However, this gradient of nanowires may decrease the carrier transport and then affect the performance of OFET based on nanowires. To solve the above problem, a "metal island" structure was proposed. We tried to grow ordered nanowires by using different metal islands and

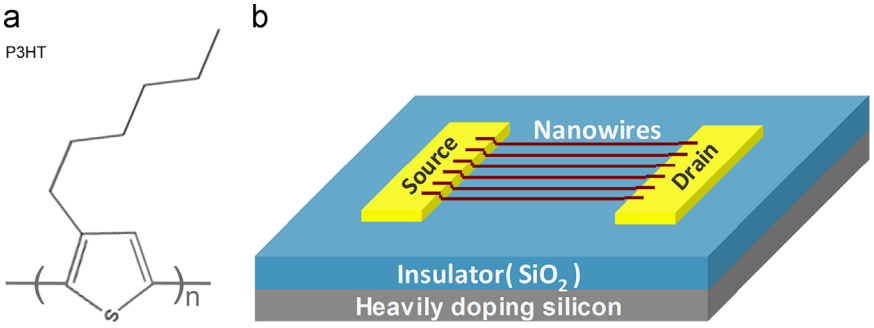

Fig. 1. (a) Chemical structure of P3HT polymer and (b) The schematic diagram of OFET based on P3HT ordered nanowire.