Thin Solid Films 646 (2018) 112–116

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Behavior of carrier transports and responsivity to solar irradiation for poly(3-hexylthiophene)/silicon devices with and without the insertion of silicon nanowires and the addition of black phosphorus

Yow-Jon Lin[a,*], Hong-Zhi Lin[a], Hsing-Cheng Chang[b], Ya-Hui Chen[c]

[a] Institute of Photonics, National Changhua University of Education, Changhua 500, Taiwan
[b] Department of Automatic Control Engineering, Feng Chia University, Taichung 407, Taiwan
[c] Precision Instrument Support Center, Feng Chia University, Taichung 407, Taiwan

ARTICLE INFO

Keywords:
Nanostructure
Polymers
Two-dimensional materials
Electrical properties
Optoelectronic properties
Heterojunction

ABSTRACT

The effects of the insertion of the silicon nanowire (SiNW) array and the incorporation of black phosphorus (BP) powders into poly(3-hexylthiophene) (P3HT) on the behavior of carrier transports and the responsivity to solar irradiation for P3HT/n-type Si (n-Si) devices are studied. It is found that thermionic emission and space charge limited current influence the forward current–voltage characteristics of P3HT/n-type Si devices. However, for P3HT/SiNWs/n-Si or P3HT:BP/SiNWs/n-Si devices, carrier transport in the forward-voltage region is dominated by ohmic conduction. In contrast with the P3HT/n-Si device, the P3HT:BP/SiNWs/n-Si device exhibits the lower reflectance, poorer rectification behavior and higher responsivity to solar irradiation, indicating that the increased photocurrent density can be interpreted by the high external light injection efficiency and the high carrier mobility in the P3HT:BP layer.

1. Introduction

Most solid state electronic devices incorporate at least one interface between a p-type semiconductor and an n-type semiconductor, hence the p-n junction is the focus of much research. The discovery of organic conducting conjugated polymers made it possible to fabricate reliable devices and sensors in ordinary laboratory conditions. There are continuous efforts to design device structures for device performance improvement. The use of heterostructures is an effective way of manipulating the electronic and optoelectronic properties of semiconductor devices. Heterojunction devices are commonly made of p-type semiconductors combined with n-type Si (n-Si) structures [1–6]. Si has been a popular material of choice because it is very abundant, non-toxic. Among many conductive polymers, the beneficial properties of poly(3-hexylthiophene) (P3HT), such as high power conversion efficiency, excellent stability, and high flexibility, have attracted significant interest for application in organic/inorganic heterojunction devices [7–11]. In this study, we introduced the techniques of the insertion of the silicon nanowire (SiNW) array and the incorporation of black phosphorus (BP) powders into P3HT (referred to as P3HT:BP) to enhance the responsivity to solar irradiation for the P3HT/n-Si device. Recently, a conceptually novel layered semiconducting material, BP, with its unique structure and intriguing electronic and optical properties, has become a new focus of two-dimensional material research [12]. Previous studies showed that BP has high carrier mobility combined with the tunable direct gap from 0.3 to 2.0 eV with decreasing thickness to a monolayer [12–14]. In order to achieve high carrier mobility in P3HT, BP is considered as a dopant for P3HT. The effect of incorporation of BP into P3HT on the electrical resistivity was investigated by Lin and Lin [15]. It is shown that the hole mobility increases significantly while the hole concentration does not substantially change [15]. The SiNWs have been the focus of extensive study during the past 15 years because of their potential for applications in electronics, sensing, photovoltaics, and photonics [16,17]. The remarkably low broadband reflectance is a major advantage of the cost-effective SiNW-based sensors. Here, we investigated the electrical and optoelectronic properties of the P3HT/n-Si, P3HT/SiNWs/n-Si and P3HT:BP/SiNWs/n-Si devices. The organic/inorganic rectifying contact fabrication and the subsequent extraction of the contact parameters is an attractive research field for realization of electronic and optoelectronic devices. Applications of P3HT/Si heterostructures to the optoelectronic devices have been reported [7,9,15,18]. To date, there have been no reports of the fabrication and characterization of P3HT:BP/SiNWs/n-Si devices.

---

* Corresponding author.
E-mail address: rzr2390@yahoo.com.tw (Y.-J. Lin).

https://doi.org/10.1016/j.tsf.2017.11.041
Received 18 August 2017; Received in revised form 12 November 2017; Accepted 30 November 2017

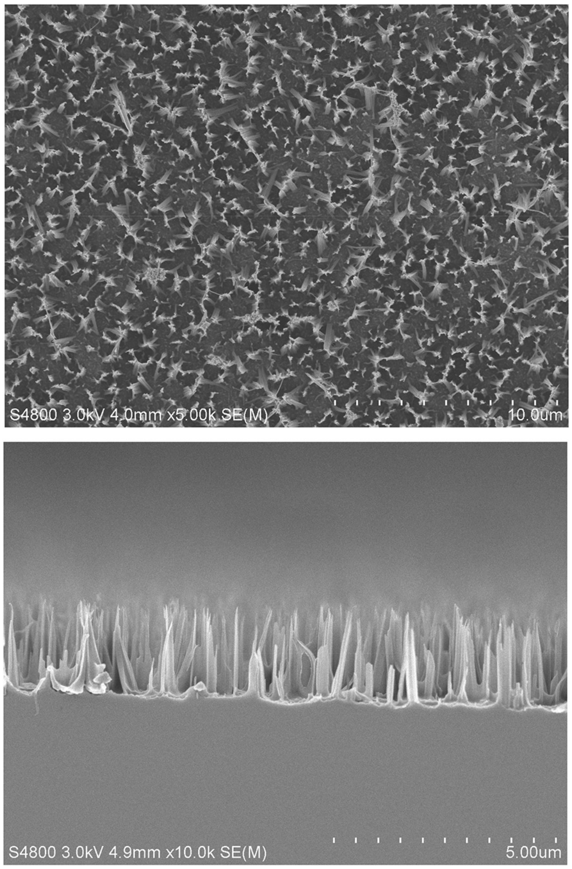

Fig. 1. Plane and cross-sectional FESEM images of the SiNWs.

2. Experimental procedure

Four-inch Si (100) wafers of n-type purchased from Guv Team International Co., Ltd. were used in the experiment. The resistivity of the 525-μm thick n-Si wafer is about 3 Ω cm. The n-Si substrates were ultrasonically cleaned for 10 min each in acetone, then in methanol, then in de-ionized water and dried in nitrogen. The SiNW arrays were then formed adopting a developed silver-induced wet-chemical-etching process in an aqueous buffered HF and $AgNO_3$ etching solution at 25 °C [19,20]. The detailed growth process is shown in Refs. 21–24. The etching time was 25 min. The SiNW length, as estimated from field emission scanning electron microscopy (FESEM), was about 1.9 μm. Fig. 1 shows the cross-sectional and plane FESEM images of the SiNWs. P3HT was purchased from Luminescence Technology Corp. BP powders were purchased from Weistron. Composite samples were prepared by adding P3HT (400 mg) to 1,2-dichlorobenzene (20 mL) solutions with/without BP powders (10 mg) addition in a nitrogen-filled glovebox. These solutions were stirred using a magnetic stirrer for 24 h at 40 °C. Then, P3HT was respectively deposited on the SiNW and n-Si surfaces and P3HT:BP was deposited on the SiNW surfaces by spin coating in a nitrogen-filled glovebox. Spin coating was performed at 600 rpm for 30 s. After depositing by spin coating, the films were baked at 55 °C for 25 min on a hotplate in a nitrogen-filled glovebox. Fig. 2 shows cross-sectional and plane FESEM images of the P3HT/SiNWs sample. Au ohmic contacts with interdigitated patterns (0.482 cm^2) were deposited onto the P3HT (P3HT:BP) surface (4 cm^2) by a sputter coater and In ohmic contacts with a square pattern (4 cm^2) were deposited onto the n-Si back surface by a sputter coater. The current–time (I–t) and current–voltage (I–V) curves were measured using a Keithley Model-4200 semiconductor characterization system at room temperature. The photo-response for the device was measured at 100 mW/cm^2, and illumination intensity from a 150 W solar simulator with an AM 1.5G filter. The photo-response was measured by recording the current versus time while sunlight illumination was turned on and off by a shutter. In order to obtain the carrier mobility and carrier concentration for P3HT or P3HT:BP films, the Van der Pauw–Hall measurements (Ecopia HMS-3000) were performed at room temperature. P3HT and P3HT:BP were deposited on glass surfaces. The electrodes were fabricated by depositing Au metal onto the P3HT or P3HT:BP layers through a shadow mask. The HMS-3000 includes software with an I–V curve that is capable of checking the ohmic integrity of the user-made sample contacts.

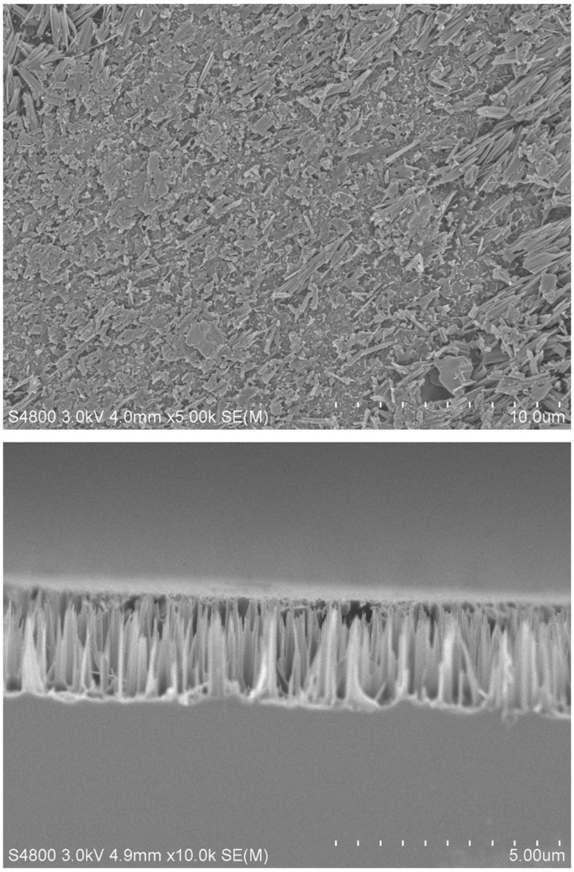

Fig. 2. Plane and cross-sectional FESEM images of the P3HT/SiNWs samples.

3. Results and discussion

Fig. 3 shows the rectification |I|–V characteristics of the P3HT/n-Si, P3HT/SiNWs/n-Si and P3HT:BP/SiNWs/n-Si devices in the dark. The result in Fig. 3 shows that the ratio of the forward to reverse current (FR) at a bias voltage of ± 1 V is 4.4 (1.6 and 5.8) for P3HT/n-Si, (P3HT/SiNWs/n-Si and P3HT:BP/SiNWs/n-Si) devices. The derived values for FR are listed in Table 1. A probable reason for a poor rectification behavior is the existence of the large leakage current for P3HT/n-Si devices. Interface states play key roles on the electrical output of the P3HT/n-Si device. Such behavior is attributed to the induced increase in the leakage current by interface states. The value of FR of P3HT/SiNWs/n-Si devices is smaller than that of P3HT/n-Si devices. Clearly, the SiNWs affect the ratio of the forward to reverse current. Due to the large surface-to-volume ratio, the SiNWs have a high surface recombination rate [19,25]. It is believed that the value of FR has a strong relation to the larger number of charge traps in the SiNWs. The existence of trap states at the P3HT/SiNW interfaces may lead to the energy barrier lowering, owing to trapped carriers jumping between the continuous potential well. The current will flow preferentially through the lower barriers in the potential distribution. Another source of the