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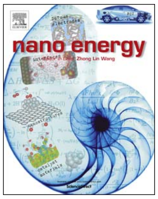

Intramolecular p-i-n junction photovoltaic device based on selectively doped carbon nanotubes

Changxin Chen[a,*], Chuanjuan Song[a], Junru Yang[b], Dingqiang Chen[a], Wenhuan Zhu[a], Chenghao Liao[a], Xusheng Dong[a], Xiaodong Liu[a], Liangming Wei[a], Nantao Hu[a], Rong He[a], Yafei Zhang[a]

[a] *National Key Laboratory of Science and Technology on Micro/Nano Fabrication, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Department of Micro/Nano Electronics, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

[b] *College of Mechanical and Electronic Engineering, Shandong University of Science and Technology, Qingdao 266590, China*

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ABSTRACT

Photovoltaic devices show promising applications in detection and energy fields as well as in next-generation optoelectronic circuits. The use of the ideal photosensitive material and device design are critical for achieving a high-performance photovoltaic device. Here, an intramolecular p-i-n junction photovoltaic device based on selectively doped carbon nanotubes is investigated. In this kind of device, the opposite ends of an individual single-walled carbon nanotube (SWCNT) channel are doped selectively by triethyloxonium hexachloroantimonate (OA) and polyethylene imine (PEI) to obtain stable p- and n- type SWCNT segments respectively, while the middle segment of the SWCNT is kept intrinsic, causing the formation of an intra-tube p-i-n junction for the efficient separation of photogenerated electron-hole pairs. The optical-absorption and electrical testing demonstrate that the OA and PEI can dope the SWCNTs into the stable *p*- and *n*- types, respectively. In the dark, the prepared p-i-n junction device behaves as a diode with a high rectification ratio $>10^3$ that can be tuned by the gate voltage. Under a 1550-nm monochromatic illumination, the device exhibits a good photovoltaic effect with a large open-circuit voltage of 0.41 V and an external power conversion efficiency of ~4.2%. The quantum efficiency of the device is estimated to be as high as ~73%.

1. Introduction

Photovoltaic devices exhibit significant application potentials in the fields of energy, sensing, and communication [1,2]. They can be applied as microcells to power micro-electro-mechanical systems (MEMS) or sensors, as highly sensitive photodetectors and as building blocks in optoelectronic circuits. Owing to their excellent electrical properties and unique one-dimensional nanostructures, single-walled carbon nanotubes (SWCNTs) are ideal candidates for fabricating photovoltaic devices. The semiconducting SWCNT had a direct bandgap that can enhance the transition efficiency of the carriers under illumination [3,4]. The bandgap of the semiconducting SWCNT can be regulated by its diameter to match the different wavelengths of the light spectrum, rendering the SWCNTs with a strong photo-absorption from the ultraviolet to the infrared range [5–7]. The electronic sub-bands of the SWCNT owing to radial quantum confinement can effectively extend the relaxation time of the hot carriers, allowing the hot carriers to be output before cooling down to enhance the photogenerated voltage. The separated sub-band structures can also produce a multi-exciton effect to increase the photogenerated current [8]. Besides, ideal SWCNTs are defect free and have an extra-high carrier mobility, greatly reducing the recombination probability of the photogenerated electron-hole pairs.

Some types of SWCNT photovoltaic devices had been reported [9–11]. A photovoltaic device with a split-gate structure in which opposite voltages were applied to the split gates for obtaining p- and n-type SWCNT segments was studied. To prepare this device, a relatively complex device fabrication process was required. We had also investigated a photovoltaic device based on asymmetrical SWCNT/metal contacts, which exhibited an open-circuit (V_{oc}) voltage of ~0.31 V and a power conversion efficiency (η) of ~0.8% under solar light. In this type of device, the built-in electric field strength was limited by the difference in the work functions of the two contact metals [12–15]. To achieve a high-performance SWCNT photovoltaic device, the ideal

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* Corresponding author.
E-mail address: chen.c.x@sjtu.edu.cn (C. Chen).

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device structure and good fabrication method are highly desired.

Here, an intramolecular p-i-n junction photovoltaic device based on selectively doped SWCNTs was investigated. In this kind of device, the opposite ends of the individual SWCNT channels were doped selectively by triethyloxonium hexachloroantimonate (OA) and polyethylene imine (PEI) to obtain stable p- and n-type SWCNT segments respectively, while the middle segment of the SWCNT was kept intrinsic, causing the formation of an intra-tube p-i-n junction. A strong built-in electric field in the SWCNTs was obtained for the efficient separation of the photo-generated electron-hole pairs. In the dark, the device behaved as a diode with a high rectification ratio of $>10^3$ that could be tuned by the gate voltage applied to the device. Under a 1550-nm monochromatic illumination, the device exhibited a good photovoltaic effect with a large V_{oc} of ~0.41 V and an external η of ~4.2%, achieved at an ~7.1 W/cm^2 incident intensity. The quantum efficiency of the device was estimated to be as high as ~73%.

2. Materials and methods

2.1. Preparation of the semiconducting SWCNT solution

The semiconducting SWCNT solution (semiconductor purity ~98%) was prepared by a density gradient ultracentrifugation method using P2-SWCNTs (Carbon Solutions, Inc., Riverside, CA) [21,22]. The SWCNTs (5 mg/ml) were sonicated in a 2% sodium cholate (SC) aqueous solution in a horn sonicator at 8 W for 1 h. The SWCNT suspension was subsequently centrifuged at 13,000 rpm for 10 min to remove large SWCNT bundles or particles. Then, the surfactant concentration was regulated in the resulting SWCNT solution to 0.8% (w/v) SC and 0.2% (w/v) sodium dodecyl sulfate. A gradient maker was used to prepare a linear iodixanol concentration gradient from 15% to 30%, maintaining uniform surfactant concentrations with the 0.8% (w/v) SC and the 0.2% (w/v) sodium dodecyl sulfate. A SWCNT solution with the same SC and sodium dodecyl sulfate concentrations (SDS) was inserted below the gradient, where the iodixanol concentration was 32%. The remainder of the centrifuge tube was filled with an overlayer of 0.8% (w/v) SC and 0.2% (w/v) sodium dodecyl sulfate. The prepared gradient solution was centrifuged at 31,000 rpm for 20 h. Then, the fractions in the centrifuge tube were extracted and dialyzed to obtain SWCNT solutions with 1% SC. The fractions with the enriched semiconducting SWCNTs were identified by UV–vis–NIR absorption spectra.

2.2. Chemical doping and optical absorption measurement of the SWCNTs

The prepared solution of semiconducting SWCNTs was dropped and dried on glass slides. To dope the SWCNTs with OA, the slide with the SWCNTs was immersed in a methanol solution of the OA (50 mg OA in 5 ml methanol) for 1 h at 70 °C. The sample was then rinsed thoroughly with methanol to remove the excessive dopant molecules. To dope the SWCNTs with PEI, the slide with the SWCNTs was submerged in a 10 wt% methanol solution of PEI (average molecular weight ~25000, Aldrich chemicals) for 8 h at room temperature (25 °C). Then, the substrates were rinsed thoroughly with methanol that removed the PEI that was non-specifically adsorbed on the sample surface and left a monolayer of PEI irreversibly adsorbed on the SWCNTs. A Lambda 950 UV–vis–NIR spectrometer (PerkinElmer, USA) was used for testing the optical absorption of the SWCNTs on the slides before and after the doping.

2.3. Fabrication of FETs and photovoltaic devices based on the individual doped SWCNTs

An n-type silicon wafer with a 100-nm-thick thermally-oxide SiO_2 layer was used in the experiment. After using a HF buffer solution (28 ml of HF, 113g of NH_4F, 170 ml of H_2O, pH=6) to remove the SiO_2 layer from the unpolished (back) side of the silicon wafer, a 100-nm-thick Au film was sputtered on the back of the silicon wafer to connect with the silicon that acts as the back gate. The resulted silicon wafer was cut into chips of 1×1 cm. Then, the SWCNT solution was spin-coated on the polished side of the chips at 2500 rpm for 1 min for depositing the SWCNTs on the chips. Straight SWCNTs with lengths $>$ 3 μm were selected as the channels for the FETs by SEM. The metal Au/Ti (50 nm/2 nm) was fabricated on two ends of the SWCNTs by the electron-beam lithography and lift-off process, which acted as the source and drain of FETs. Here the thin metal Ti acted as the adhesive layer between the metal Au and the substrate. The same doping processes described for the SWCNTs on the slides were used for the p-type and n-type doping of the SWCNT channels in the FET.

To fabricate the p-i-n junction devices, a selective doping method was performed. First, a 200-nm-thick PMMA resist (molecular weight: 950 k) was spin-coated on the above-mentioned devices with a channel length of ~1.9 μm for protecting the device. Using e-beam lithography and a lift-off process, a rectangular window with 1 μm in width parallel to the SWCNT length direction and 2 μm in length perpendicular to the SWCNT length direction was opened at one end of the SWCNT channel. The window opened had an overlap of 0.3 μm in the width direction with the contact electrode and contained a CNT channel length of 0.7 μm. Then, the chip was submerged in a 10 wt% methanol solution of PEI (average molecular weight ~25000, Aldrich chemicals) for 8 h at room temperature (25 °C), followed by a thorough rinsing of the device with methanol. The PMMA resist was then removed by acetone. Similarly, a PMMA window (1×2 μm) was fabricated to expose the opposite end of the SWCNT channel, which contained a CNT channel length of 0.7 μm and had an overlap of 0.3 μm in the width direction with the contact electrode. The chip was soaked in OA solution (50 mg OA in 5 ml methanol) for 1 h at 70 °C, followed by a thorough rinsing of the device with methanol. Then, the PMMA resist was removed by acetone. Meanwhile, the middle segment (~0.6 μm in length) of the SWCNT channel was protected by the PMMA resist and kept intrinsic. Thus, an intramolecular p-i-n junction photovoltaic device was fabricated.

2.4. Measurement of the SWCNT-based FETs and p-i-n junction photovoltaic devices

An Agilent 4156 C semiconductor parameter analyzer (Agilent Technologies Inc., Santa Clara, CA, USA) was used for testing the electrical performance of both kinds of devices at room temperature (25 °C). In the electrical measurement of the p-i-n junction photovoltaic devices, the bias was applied to the electrode contacting with the p-doped SWCNT segment, while the electrode connecting with the n-doped SWCNT segment was grounded.

The characteristics of the p-i-n junction photovoltaic device were measured using a 1550-nm (0.8 eV) laser transmitted via an optical fiber, which had a spot diameter of ~9 μm. Considering that the 1550-nm laser was invisible, the 633-nm and 1550-nm lasers were coupled to the same optical fiber and a visible 633-nm laser was used to pre-focus the laser beam on the functional area of the device for guiding the illumination of the 1550-nm laser. The illumination direction of the laser was perpendicular to the silicon chip, at a distance of ~10 mm from the device.

3. Results and discussion

The prepared semiconducting SWCNT solution with an average tube diameter of 1.4 nm was characterized by the Raman spectra, in which a 532-nm laser was used as the excitation light. In Fig. 1a, a sharp G-band and a high intensity ratio (~50) of G-band to D-band were observed in the Raman spectrum, indicating that the graphitization degree of the SWCNTs was high and that there were very few

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