Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 106 (2014) 171–176

SOLAR ENERGY

www.elsevier.com/locate/solener

Acid-doped multi-wall carbon nanotube/n-Si heterojunctions for enhanced light harvesting

Muatez Mohammed [a,b], Zhongrui Li [c,d,*], Jingbiao Cui [a], Tar-pin Chen [a,*]

[a] Department of Applied Science, Department of Physics and Astronomy, University of Arkansas at Little Rock and Green Solar Cell Research, AR 72204, United States
[b] College of Science, University of Al-Qadisiyah, Al-Qadsiyah, Iraq
[c] High Performance Materials Institute, Florida State University, Tallahassee, FL 32310, United States
[d] Electron Microbeam Analysis Laboratory, University of Michigan, MI 48109, United States

Received 24 October 2013; received in revised form 31 January 2014; accepted 10 March 2014
Available online 8 April 2014

Communicated by: Associate Editor Dr. Sam-Shajin Sun

Abstract

Multiple wall carbon nanotube (MWNT) networks form Schottky-like heterojunction on n-type silicon substrate. Acid doping downshifts the Fermi level of the MWNTs, can significantly reduce the internal resistance of the MWNT film. Wetting the MWNT networks with nitric or sulfuric acid can form MWNT-acid–Si photoelectrochemical units. The photoelectrochemical units and the Si–MWNT heterojunctions connected in parallel on the same side of the Si substrate, consequently boosting the power conversion efficiency by more than 10 times.

Keywords: Carbon nanotube solar cells; MWNT/Si; Nitric acid; Sulfuric acid; Acid infiltration; Photoelectrochemical cells

1. Introduction

Carbon nanotubes (CNTs) prove to be potentially ideal material for photovoltaic applications thanks to their strong and tunable optical absorptivity, ultrafast exciton/charge transport, and economical solution-processability (Hagen and Hertel, 2003; Fuhrer and Kim, 2002). Semiconducting tubes with different diameter can absorb photons in the full solar spectrum from infrared to ultraviolet (Odom et al., 1998; Pedersen, 2003). Charge carrier in the tubes can ballistically transport without scattering (Freitag et al., 2004). High aspect ratio and flexibility enable CNTs to be weaved into two-dimensional networks with tunable electrical and optical properties, which can be easily coated on the surface of various semiconductors. Coating CNT film on an n-type Si substrate can form CNT/Si heterojunction and can be used for photon sensing and light harvesting (Wei et al., 2007). This configuration can avoid metal wiring from the device surface that blocks a portion of incident light, since charge collection and transport can be realized by the transparent electrode made of the two-dimensional conductive CNT network. The efficiency of the CNT/Si solar cells can be optimized by tailoring the composition (metallic tubes *versus* semiconducting tubes), the thickness of the CNT film, and even by the post-treatments.

Despite the high promise of this configuration, many technical issues remain to be solved to make CNT/Si solar cells more viable for practical applications. The power-conversion efficiency of such solar cells needs to be further

---

* Corresponding authors. Address: High Performance Materials Institute, Florida State University, Tallahassee, FL 32310, United States.
E-mail addresses: zli3@fsu.edu (Z. Li), txchen@ualr.edu (T.-p. Chen).

http://dx.doi.org/10.1016/j.solener.2014.03.014
0038-092X/© 2014 Elsevier Ltd. All rights reserved.

improved through a cost-effective process. One simple approach to improve the conversion efficiency is to wet the CNT/Si interface with acid solution (Jia et al., 2011; Wadhwa et al., 2011). $SOCl_2$-post treatment has been reported to be able to improve single wall carbon nanotube (SWNT) devices by more than 45% (Li et al., 2008). 13.8% efficiency solar cells have been fabricated by infiltrating SWNT/n-Si with dilute HNO_3 (Jia et al., 2011). However, to date no literature reports about multi-wall carbon nanotube (MWNT)/Si devices and the acid treatment effect on their performance. As compared with single-wall counterparts, MWNTs are mechanically much stronger, and available at large quantity and much lower cost. The surface property of MWNTs can be altered through functionalization of the outer wall while keep the inner walls intact. In this work, we fabricated MWNT/Si hybrid solar cells and systematically studied the influence of different acid treatment of MWNT network on the electrical and optical properties as well as the photovoltaic performance of the MWNT/Si devices. It was found that infiltration of a dilute acid (such as HNO_3, H_2SO_4) on MWNT films can significantly reduce internal resistance, assist charge carrier separation, boost the transport efficiency, and enhance the power conversion efficiency of the MWNT/n-Si devices.

2. Materials and methods

MWNTs used in this work were synthesized from the pyrolysis of acetylene at 720 °C on a $Fe_2Co/CaCO_3$ catalyst (Fe and Co take 5 wt% of the total catalyst weight) as described elsewhere (Li et al., 2008). The as-produced mixture was purified by removing catalyst support CaO and Fe–Co metal particles through hydrochloric acid treatment with the assistance of sonication. The purified MWNTs were achieved after filtration and washing, and then dispersed in pure dimethylformamide solution (DMF, 0.5 mg/mL) for sonication. The MWNT/DMF solution was sprayed on n-type silicon wafers (resistivity = 0.295 Ohm cm, mobility = 1026 cm^2/V s) and glass substrates (for reference). These n-type silicon wafers with a window of pre-deposited insulating layer were placed on a heating platform side by side with a glass substrate so that the resulting MWNT films on Si and glass substrates would have same thickness. The DMF solvent was removed from the coatings by heating the device up to 150 °C. Then the MWNT coatings were immersed into H_2SO_4 (1 N) and HNO_3 (1 N) solution for one hour for acid treatment. The schematic diagram is shown in Fig. 1.

The morphology of the purified MWNTs was examined by scanning electron microscopy (SEM) performed on a JEOL 7000F high-resolution scanning electron microscope with an accelerating voltage of 15 kV. Elemental analysis was performed using an EDAX Genesis EDS system. Raman scattering signal from the MWNTs were collected at room temperature using a Horiba Jobin Yvon LabRam HR800 spectrometer equipped with a grating of 600 lines/mm and a charge-coupled detector. A He–Ne laser (633 nm) was used as excitation sources. Raman shifts were calibrated by the 521 cm^{-1} peak of a silicon wafer. The photoluminescence (PL) spectra under different excitation wavelengths were carried out at room temperature by a Horiba Jobin Yvon 320 spectrometer. The PL excitation source is a He–Cd laser with wavelength of 325 nm. The emission light was focused onto the entrance of a monochromator and detected by a CCD camera. Electrochemical impedance spectra (EIS) of the solar cells were measured at the frequency range of 0.005–1 MHz under the alternative signal of 10 mV. The impedance measurements were carried out at 0.3 V. The photovoltaic performance of the devices was characterized by measuring the *I–V* characteristic curves of the devices both in dark and under AM1.5 illumination (~100 mW/cm^2). The devices were irradiated in an area of 5 × 5 mm^2 under a small-area class-B solar simulator (PV Measurements, Inc.), and the data were recorded using a Keithley 2400.

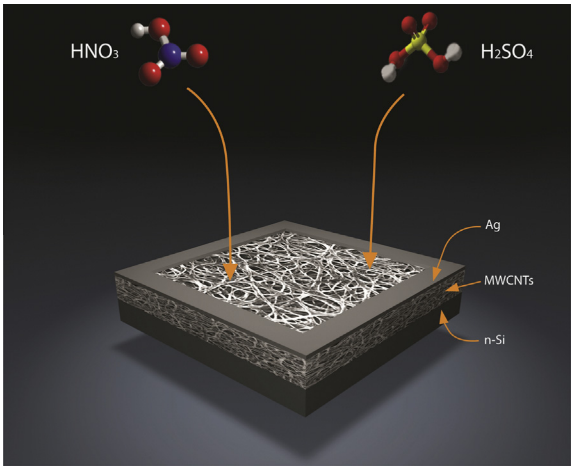

Fig. 1. Schematic diagram of an acid-wetted MWNT/n-Si device.

3. Results and discussion

The morphology of the MWNTs used in this work that was examined by using SEM (Fig. 2a). More than 95% of the nanotube bundles have diameters between 5 and 25 nm and length from 5 to 60 μm. The purity of the carbon nanotubes was evaluated by using thermogravimetric analysis (TGA). The weight loss profile in Fig. 2b was obtained by heating the purified MWNTs from room temperature to 850 °C at a rate of 5 °C/min. The normalized TGA curves and their first derivative (dW/dT) indicate a significant mass loss around 594 °C for the MWNTs. The narrow width (~83 °C) of the derivative (dW/dT) shown in Fig. 2b reflects the good crystallinity as well as the narrow diameter distribution of the nanotubes, since thin and defective nanotubes usually have a lower combustion temperature. A quantitative analysis revealed that the purity of the MWNT material is up to 98.2%. The impurities are trace amount of amorphous carbon (<1 wt%) and metal oxides/carbides (<1 wt%).