p-Type Single-Wall Carbon Nanotube Network on n-Type Si for Heterojunction Photovoltaic Cells

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ABSTRACT

High-density p-n heterojunctions between single wall carbon nanotubes (SWNTs) and n-type crystalline silicon produced with airbrushing technique were used for light harvesting. The SWNT/n-Si heterojunction is rectifying. Under illumination the numerous heterojunctions formed between the semitransparent SWNT thin coating and the n-type silicon substrate generate electron-hole pairs, which are then split and transported through SWNTs (holes) and n-Si (electrons), respectively. The nanotubes serve as both photogeneration sites and a charge carriers collecting and transport layer. It was also found that the thionyl chloride (SOCl2)-treatment of SWNT coating films can lead to a significant increase in the conversion efficiency through readjusting the Fermi level and increasing the carrier concentration and mobility of the nanotube network. Initial tests have shown a power conversion efficiency of above 4%, proving that SOCl2 treated-SWNT/n-Si is a potentially suitable configuration for making solar cells.

Keywords: SWNT, p-n heterojunction, solar cell

1 INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have a wide range of direct bandgaps matching the solar spectrum,1,2 and show strong photoabsorption from infrared to ultraviolet,3,4 and exhibit high carrier mobility5 and reduced carrier transport scattering.6 These superior properties of SWNTs have also made them potential materials for highly active photovoltaic devices.7 Photovoltaic effect can be achieved in carbon nanotube based p-n junction diodes.8 Under illumination, the SWNT diodes demonstrate significant power conversion efficiencies owing to enhanced properties of an ideal diode. A single device element that contains an ensemble of defect-free and electronically isolated semiconducting SWNTs is required for many real-world applications. A device consisting of a large number of tubes provides good device-to-device uniformity, even if the properties of individual tubes are heterogeneous. More importantly, current carrying capability increases with increasing tube density.9 High-density carbon nanotubes are needed for achieving sufficiently high total surface area for light sensing applications. A SWNT-based photovoltaic device requires high-density SWNTs to efficiently capture light.

In this work, we designed and tested simple photovoltaic devices which consist of a semitransparent thin film of nanotubes conformally deposited on an n-type crystalline silicon substrate to create high-density p-n heterojunctions between nanotubes and n-Si to favor charge separation and extract electrons and holes. Furthermore, the post-treatment of the SWNT coating film with thionyl chloride (SOCl2) can considerably improve the photovoltaic properties of the heterogeneous junctions.

2 EXPERIMENTAL SECTION

Fabrication of SWNT/n-Si heterojunctions: The small diameter SWNTs were synthesized from CO proportionation over Co-Mo/SiO2 catalyst.10 The purified SWNTs were dissolved in dimethylformamide (DMF, 0.5 mg/mL) with the assistance of sonication, and the uniform solution was directly sprayed on silicon wafers by means of an airbrush using dry air as carrier gas. A silicon wafer with a window of predeposited insulating layer and a glass substrate (for reference) were placed on a heating platform side by side and heated up to 150 °C in order to evaporate the DMF solvent from the film. Schematic diagram of a SWNT/n-Si solar cell was displayed in Figure 1a.

Device Characterization: Optical transmission was chosen as an appropriate method of averaging the structural irregularities and characterizing the thickness of various thin SWNT networks prepared on a glass substrate. The temperature dependent conductivity measurements were performed for the reference SWNT films. The Hall Effect measurements were performed under magnetic field of 0.2 T by using standard van der Pauw geometry. To perform the photovoltaic testing, the devices were irradiated under a small-area class-B solar simulator (PV Measurements, Inc.) at AM1.5 (~100 mW/cm²), and data were recorded using a Keithley 2400.

3 RESULT AND DISCUSSION

3.1 Thickness effect of SWNT coating on photovoltaic conversion
Figure 1. (a) Schematic diagram of a SWNT/n-Si solar cell. (b) SEM image of a SWNT film showing porous network structure, SWNT bundles in close contact to the Si surface. The morphology of these coatings can be described as a randomly distributed network of SWNTs with a high density of void spaces.

Figure 2. Optical transmission property of a SWNT reference film. Inset: Optoelectronic performance of SWNT films with different thickness at wavelength of 600 nm. Two structures, (6,5) and (7,5) together dominate the semiconducting nanotube distribution and comprise more than half of the population.

The networks of SWNTs lying on the substrate surface form agglomerates of nanotube bundles containing many tubes alternating with empty regions (Figure 1). Therefore, it is difficult to define the thickness of these networks. Optical transmission was chosen as an appropriate method of averaging the structural irregularities and characterizing the thickness of various thin SWNT networks prepared on a glass substrate. As seen in the optical absorption spectrum (Figure 2), two structures, (6,5) and (7,5) together dominate the semiconducting nanotube distribution and comprise more than half of the population. The transmittance values measured on our five transparent networks at wavelength of 600 nm are given in the inset of Figure 2b. Such semitransparency ensures the absorption of the solar light by both the SWNT film and the underlying Si wafer. Four-probe measurements for the SWNT films show that sheet resistance varies from 250 to 3900 Ω/sq for SWNT films with transmittance of 51-86% at wave length of 600 nm. Thus, our SWNT films can be directly used as a transparent conductive layer for solar cells, which can simplify the fabricating process of the SWNT solar cell.

Figure 3. (a) Current-voltage plot of a typical SWNT/n-Si device in dark and under illumination, showing typical solar cell performance with efficiency of 2.7%. (b) Schematic energy band diagram of the heterojunction diode.
showing the photogenerated carrier transfer process. (c) Summary of short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($f$), and efficiency ($\eta$) for SWNT cells with different thickness, showing maximum current and efficiency of the device with transmittance of around 60%.

Figure 3a shows the current-voltage characteristics of a typical SWNT/n-Si solar cell, in which the SWNT film has about 60% transmittance (at 600 nm), in dark and under white light illumination (AM1.5, ~100 mW/cm$^2$). The device shows an evident p-n junction behavior in the dark, where the reversed current density is very low (~30 $\mu$A/cm$^2$, over 400 times lower than the forward current density) when the bias voltage sweeps from -1.0 to 0 V compared to forward current (~13 mA/cm$^2$ at 1.0 V) as shown in Figure 3a. Under illumination, the I-V curve shifts downward, with an open-circuit voltage $V_{oc}$ and short-circuit current density $J_{sc}$ of about 0.5 V and 21.8 mA/cm$^2$, respectively. The fill factor ($f$) and power efficiency ($\eta$) of our devices show a fill factor in similar range but much higher efficiency.

SWNTs usually behave as p-type semiconductors, indicating that large amount of holes in SWNTs are available. When fully expanded on a planar Si substrate, there will be numerous p-n junctions formed due to close contact between SWNTs and underlying n-Si. The I-V curve in the dark actually shows a typical diode behavior, further confirming the existence of p-n junction of this SWNTs-on-Si configuration (Figure 3a). The rectifying behavior in the dark and the photocurrent phenomenon under illumination of the SWNT/n-Si heterojunction cell can be explained by the energy band structure of this heterostructure. Figure 3b shows the schematic energy band diagram of the heterojunction diode at thermal equilibrium. Since the band gaps ($E_g$) of our Si and SWNTs are 1.1 and ~2.7 eV, respectively, an asymmetrical energy barrier would be formed at the junction interface. When the device is illuminated by the simulated sunlight from the top of p-type SWNT film, photons with energy less than $E_g$(SWNT) but greater than $E_g$(Si) will transmit through the SWNT films, acting as an optical “window”, and be absorbed by the n-type Si. Part of the light can directly reach the junction via the empty space between the SWNT networks. Simultaneously, light with photon energies larger than $E_g$(Si) (SWNT) will be absorbed by the SWNTs. In our case, the semiconducting tubes (6, 5) and (7, 5) dominate the tube species distribution. So, only the photons with energies larger than the tubes’ energy gaps or/and the silicon energy gap can be absorbed and converted into electron-hole pairs (excitons). The holes and electrons generated in both sides of the heterojunction are collected effectively due to the large built-in electric field at the junction and thus yield the photocurrent as schematically shown in Figure 3b.

3.2 Enhanced Photovoltaic effect by SOCl2 functionization

To enhance the performance of the solar cells, we tried chemical doping using SOCl2, a liquid organic solvent with remarkable reactivity toward the SWNTs surfaces. The SOCl2 treatment involved dripping about 3 droplets of pure SOCl2 onto the SWNT film followed by drying in air. The chemical attachments of functionals to the SWNTs are in
the form of acyl chloride groups. Figure 4 demonstrates the effect of the SOCl$_2$-treatment on the photovoltaic and electrical properties of a SWNT/n-Si device. After the SOCl$_2$-treatment, the short circuit current jumps onto 26.5 mA/cm$^2$ from 20.7 mA/cm$^2$, and the open circuit voltage slightly increased to 0.49 V from 0.46 V, and the $f$ is raised up to 0.34 from 0.29, as a consequence, the SOCl$_2$ post treatment leads to about 60% increase in power conversion. Initial tests have shown a power conversion efficiency of above 4%.

As a strong oxidizing agent, SOCl$_2$ exhibits remarkable electron-withdrawing ability when adsorbed onto the SWNT surface. The significant charge transfer induced by SOCl$_2$ could also enable Fermi level shifting into the van Hove singularity region of SWNTs, resulting in a substantial increase in the density of states near the Fermi level. Consequently, the conductivity of the SOCl$_2$-treated SWNT films significantly increased. With this functioning technique, typical sheet conductance of the optimized films can be improved about 5-10 folds.

The carrier densities and mobilities of these SWNT films can be determined by Hall-effect measurements. The concentration of the carriers is given in terms of the sheet number $N_{2D}$ (cm$^{-2}$). After the SOCl$_2$-treatment, the carrier densities for the SWNT film increased from $3.1 \times 10^{15}$ to $4.6 \times 10^{17}$ cm$^{-2}$. The effective mobilities for the SWNT, SOCl$_2$-SWNT films and n-Si are 0.21, 1.72, and 1026 cm$^2$ V$^{-1}$s$^{-1}$ respectively. Interestingly, the SOCl$_2$ treatment can significantly enhance the SWNT mobility. The low mobility of the SWNT network could be caused by several factors including high resistivity between SWNT bundles and Schottky barriers between semiconducting and metallic nanotubes. The Hall effect measurements show that all SWNT film samples show p-type conductivity. A standard oxidative purification process is known to induce p-type charge-transfer doping of the nanotubes. This, along with doping from atmospheric impurities, is thought to influence the optoelectronic performances of the films. Transparent SWNT films are hole conducting, simple to fabricate, flexible and low cost. Hence, they would be highly beneficial for the next generation of solar cells.

4 CONCLUSION

In brief, high dense SWNT/n-Si heterojunctions prepared with a simple airbrushing technique show a strong rectifying behavior and photovoltaic effect when optically excited. SWNTs can be directly used as the energy conversion materials in solar cells, serving for both the photogeneration process and charge carrier transport. The numerous heterojunctions formed between p-SWNTs and n-Si perform just as the conventional p-n junctions in the generation of electron-hole pairs, which are then split and transported through SWNTs (holes) and n-Si (electrons), respectively. The SOCl$_2$-treatment of SWNT films leads to significant increase in the conversion efficiency by adjusting the Fermi level and enhancing the carrier mobility of the SWNT coating.

REFERENCES