Carbon Nanotubes and Graphene for Solar Cells

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ABSTRACT

Carbon nanotubes and graphene represent attractive materials for photovoltaic devices. Single wall carbon nanotubes (SWNTs) and graphene layers can be directly configured as energy conversion materials to fabricate thin-film solar cells, serving as both photogeneration sites and charge carriers collecting/transport layers. SWNTs can be modified into either p-type conductor through chemical doping (like thionyl chloride, or just exposure to air) or n-type conductor through polymer functionalization. The solar cells consist of either a semitransparent thin film of p-type nanotubes (functionalized graphene) deposited on an n-type silicon wafer or a semitransparent n-type SWNT thin film on p-type substrate to create high-density p-n heterojunctions and favor charge separation and extract electrons and holes. The high aspect ratios and large surface area of carbon nano-structured materials could be beneficial to exciton dissociation and charge carrier transport thus improving the power conversion efficiency.

Keywords: photovoltaic devices, single wall carbon nanotube, graphene

1 INTRODUCTION

Semiconducting single wall carbon nanotubes (SWNTs) are potentially ideal material for photovoltaic applications thanks to their superior properties such as a wide range of direct bandgaps matching the solar spectrum [1], strong photoabsorption [2,3] from infrared to ultraviolet, and high carrier mobility [4] and reduced carrier transport scattering [5]. A standard oxidative purification process is known to induce p-type charge-transfer doping of SWNTs [6], so it is easy to fabricate p-type SWNT solar cells. It is possible to fabricate n-type SWNTs by doping low work function metals (like Al) onto the tubes [7] or through nitrogen doping of metallic SWNTs [8]. Graphene has shown remarkable photonic properties, such as high transparency and wide absorption spectral range, as well as outstanding electronic and mechanical properties, so extensive interest has developed toward applying it to optoelectronic devices. Unlike SWNTs, which contain 1/3 metallic species, narrow graphene nanoribbons (<10 nm) are semiconducting due to their edge effects [9]. Charge carriers in graphene behave as massless relativistic particles (Dirac fermions) and exhibit ballistic transport on the sub-micrometer scale at room temperature. Graphene combines high electron mobility with atomic thickness. Theoretic studies show that the substitutional doping can modulate the band structure of graphene [10], leading to a metal-semiconductor transition [11]. In this work, we designed and tested simple photovoltaic devices based on the high density heterojunctions formed between either acid purified or polymer functionalized SWNTs or graphene and different type semiconductor substrates.

2 EXPERIMENTAL

The CoMoCat SWNTs were utilized as photovoltaic media [12]. (1) To fabricate SWNT/n-Si device, the purified SWNTs were first dissolved in dimethylformamide (DMF, 0.5 mg/mL) under sonication, and the uniform solution was directly sprayed on n-type silicon wafers by airbrushing. A silicon wafer with a window of predeposited insulating layer was placed on a heating platform and heated up to 150 °C in order to evaporate the DMF solvent from the film. (2) To make PEI-SWNT/p-Si cells, the purified SWNTs were submerged in a 10 wt% solution of polyethylene imine (PEI, average molecular weight ~2000) in methanol overnight, followed by rinsing with methanol. This removed PEI nonspecifically adsorbed on the sample surface, leaving nearly a monolayer of PEI irreversibly adsorbed on tubes as described below. The PEI-functionalized SWNTs (PEI-SWNT) were dispersed in dimethylformamide (DMF, 0.5 mg/mL) under sonication, and the uniform solution was directly airbrushed onto p-type silicon substrate (p-Si) which was heated up to 150 °C. (3) For the preparation of acid treated graphene/n-Si device, graphene (1-2 layers, Angstrom Materials LLC) was sonicated at 40 °C in 120 mL of a 3:1 mixture of H2SO4 and HNO3 for 6 h, and the dispersion was allowed to stand for 4 days. After repeated washing with water, the oxidized graphene was filtered, and further dispersed in SOCl2 at 70 °C for 2 days. At the end of reaction the excess SOCl2 was removed by distillation. The product was dissolved in DMF and airbrushed onto a silicon wafer with a window of pre-deposited insulating layer under heating.

3. RESULTS AND DISCUSSION

3.1 p-type SWNT/n-type Si solar cells

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The randomly distributed networks of SWNTs containing many well-aligned tubes alternating with empty regions (Figure 1a, inset) are coated on the Si substrates, showing structural irregularity. In this work optical transmission was used to characterize the thickness of various thin SWNT networks prepared on a glass substrate. The film thickness can be controlled to reach hundreds of nanometers by using different number of airbrushing strokes. The SWNT films show sheet resistance varying from 250 to 3900 Ω/sq for SWNT films with transmittance of 51-86% at wavelength of 550 nm. Thus, the SWNT films can be directly used as a transparent conductive layer for solar cells, which can simplify the fabrication process of the SWNT solar cell.

Figure 1: (a) Optoelectronic performance of SWNT films with different thickness at wavelength of 550 nm. Inset (bottom) shows the top view SEM image of a device. (b) 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 about 60%. (c) The effect of the thionyl chloride (SOCl₂) treatment on the photovoltaic performance of SWNT/n-Si heterogeneous junctions.

The flexibility of the fabrication process allows the construction cell devices containing SWNT films with different thickness by controlling the airbrushing process. We have made cells with tailored SWNT coating thicknesses roughly ranging from 30 to about 270 nm (corresponding to 86-51% transmittance). All the cells show relatively stable voltages ($V_{oc}$) ranging from 0.37 to 0.45 V, but quite different current densities ($J_{sc}$) (Figure 2b). Increasing SWNT network density can increase the total area of SWNT-Si junctions in the device, which could enhance the current generation/transport. The cell with transmittance of ~60% shows the highest $J_{sc}$ (21.8 mA/cm²) and $\eta$ (2.7%). At further increased film thickness, the values of $J_{sc}$ and $\eta$ decrease significantly. For the thicker coating ($T > 60\%$), the SWNTs at top layers are suspending on the underneath layers and cannot touch the Si substrate to form junctions. Also, thicker films are less transparent, preventing more incident light from reaching the substrate. The devices have the potential to be further optimized, for example, by tailoring the bundle size (dispersion) and the semiconducting to metallic tubes ratio of SWNTs, so that power conversion efficiency can be further improved.

The excellent photovoltaic performance of the SWNT solar cell originates from the numerous heterojunctions created at the interface between the SWNT film and the n-Si [13]. Acid purified SWNTs usually behave as p-type semiconductors [14]. 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. 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. 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. 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, where electrons are directed to the n-type Si region and holes are transported through the SWNTs, and thus yield the photocurrent. The high $J_{sc}$ of the solar cells suggests that the presence of high density p-n junctions significantly enhanced the generation and transport of charge carriers from both SWNTs and silicon under light irradiation. Nanotubes act mainly as hole collectors and conductors in polymer/nanotube solar cells [15]. In our SWNT/n-Si devices, SWNTs might have participated in the photogeneration process as well as charge transport, and their high mobility ensures much
enhanced efficiency compared with polymer composite cell structures. The high aspect ratios and large surface area of nanotubes can help exciton dissociation and charge carrier transport, accordingly the power conversion efficiency gets improved.

To enhance the performance of the solar cells, we carried out 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 films followed by drying in air. The chemical attachments of functionals to the SWNTs are in the form of acyl chloride groups. Figure 1c demonstrates the effect of the SOCl₂-treatment on the photovoltaic and electrical properties of a SWNT/n-Si device. After the SOCl₂ treatment, the $J_{sc}$ jumps onto 26.5 mA/cm² from 20.7 mA/cm², and the $V_{oc}$ slightly increased to 0.49 V from 0.46 V, and the $f$ is raised up to 0.35 from 0.29, as a consequence, the SOCl₂ post treatment leads to 59% increase in power conversion. Initial tests have shown a power conversion efficiency of about 4.5%.

The conductivity of the pristine SWNT films can be significantly increased by SOCl₂-treatment [16]. As a strong oxidizing agent, SOCl₂ exhibits remarkable electron-withdrawing ability when adsorbed onto the SWNT surface. The significant charge transfer induced by SOCl₂ 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. With this functioning technique, typical sheet conductance of the SWNT films can be improved about 5-10 folds. In our configuration, SWNTs act as photogenerator as well as charge transporter. Semiconducting tubes would benefit photogeneration process but have poor conductivity; on the contrary, metallic tubes contribute more charge transportation but less photogeneration. Since SOCl₂ treatment can significantly improve the conductivity of semiconducting SWNT film, metallic tubes play less important role in the photoconversion of the SOCl₂-enhanced SWNT/n-Si device.

### 3.2 n-type SWNT/p-type Si

Figure 2 shows the current-voltage characteristics of a typical PEI-SWNT/p-Si solar cell, in which the SWNT film has about 30% transmittance at wavelength of 550 nm, in dark and under white light illumination (AM1.5, ~1000 W/m²). A rectifying behavior is observed in PEI-SWNT/p-Si: the current is blocked when the PEI-SWNT is biased oppositely but starts to increase while the polarity is switched to the negative. Therefore the device is at forward (reverse) bias when the voltage applied to PEI-SWNT is negative (positive). Under illumination, the blend device shows an open-circuit voltage $V_{oc}$ of about 0.42 V, short-circuit current density $J_{sc}$ of 0.45 A/m², and fill factor of 0.16. The above results lead to several important conclusions: (1) PEI irreversibly adsorbs onto the sidewalls of SWNTs, and the adsorbed PEI is capable of and responsible for n-doping of SWNTs. The high density of electron donating amine functionalities in PEI brings about significant n-doping to a level where the adverse effect of p-doping by O₂ adsorption is overcome. (2) There will be numerous p-n junctions formed due to close contact between PEI-SWNTs and underlying p-Si substrate. 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), which were subsequently diffused to the depletion region of SWNT-Si junctions and separated. (3) The PEI-SWNT film can be directly used as a transparent conductive layer for solar cells, which can simplify the fabricating process of the CNT solar cell.

Figure 3 shows the I-V characteristics of a typical PEI-SWNT/p-Si device in dark (solid blue) and under illumination (doted red) before and after 12 h UV irradiation. The inset (bottom) displays the schematic diagram of a PEI-SWNT/p-Si solar cell. The inset (top) shows the resistance change of a PEI-SWNT film coated on a glass plate as a function of exposure time to UV (maximum intensity at 254 nm) irradiation in N₂ atmosphere.

Exposure of SWNTs to ultraviolet (UV) light results in efficient molecular photodesorption from SWNTs. Photodesorption of oxygen from the PEI-coated SWNTs renders nanotubes to higher n-doping levels. Figure 2 inset (top) shows that the resistance of a PEI-SWNT film decreases under UV illumination. This is due to an increase in electron density upon photoremoval of oxygen adsorbed on the nanotube prior to PEI functionalization. The increased n-doping is also clearly observed in the evolution of I-V characteristics of the PEI-SWNT/p-Si solar cell. Although the open circuit voltage basically has no change, the short circuit current and the fill factor increase to 0.51 A/m² and 0.27, respectively, upon photoremoval of oxygen.

### 3.3 Functionalized graphene/n-type Si

Figure 3 shows the I-V characteristics of a typical graphene/n-Si solar cell, in which the functionalized graphene film, in dark and under white light illumination (AM1.5, ~100 mW/cm²). The device shows an evident p-n
junction behavior in the dark, where the reversed current density is very low (< 0.1 μA/cm², 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 μA/cm² at 1.0 V). Under illumination, the I-V curve shifts downward, with an open-circuit voltage \( V_{oc} \) and short-circuit current density \( J_{sc} \) of about 0.28 V and 0.03 mA/cm², respectively. The graphene sheet represents an extreme dish-like-shape material; it has a 2D structure and a high aspect ratio. Such a structure of graphene can effectively facilitate the desired nanometer-scale donor/acceptor interface formation for charge separation and charge transfer. In general, optimal photocurrent generation requires a tradeoff between a maximization of the interfacial area between donor and acceptor and an optimized percolation through the film avoiding charge-carrier recombination losses during the charge transport [18]. The former maximizes the generation of charge carriers, while the percolation directly improves the charge transport properties. Acid functionalized graphene layers likely behave as p-type semiconductors. When fully expanded on a planar Si substrate, there will be numerous p-n junctions formed due to close contact between graphenes and underlying n-Si. 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, where electrons are directed to the n-type Si region and holes are transported through the graphenes, and thus yield the photocurrent.

Figure 3: Current-voltage plot of a functionalized-G/n-Si device under dark and illumination. Inset (top) displays schematic diagram of a functionalized graphene/n-Si solar cell. Inset (bottom) shows the top view SEM image of a device.

4. CONCLUSION

In brief, the solar cells consist of a semi-transparent thin film of the p/n-type nanotubes/graphene conformally deposited on an n/p-type crystalline Si substrate to create high-density p-n heterojunctions between carbon nanostructure materials and silicon substrates to favor charge separation and extract electrons and holes. The carbon nanomaterials were serving as both photogeneration sites and a charge carriers collecting/transport layer. It is expected that after complete development, pure carbon cells may become more economical than silicon-based solar cells, and the cost would be extremely low and, unlike silicon, it is highly chemically and environmentally stable.

ACKNOWLEDGEMENTS

This research was partially supported by the DOE (Grant No. DE-FG 36-06 GO 86072). Also the financial support from Arkansas Science and Technology Authority (ASTA) grant # 08-CAT-03 is highly appreciated.

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