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100% internal quantum efficiency in polychiral single-walled carbon nanotube bulk heterojunction/silicon solar cells

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ABSTRACT

Bulk heterojunction films made of polychiral single-walled carbon nanotubes (SWCNTs) form efficient heterojunction solar cells with n-type crystalline silicon (n-Si), due to their superior electronic, optical, and electrical properties. The films are multi-functional, since their hierarchical surface morphology provides a biomimetical anti-reflective, air-stable, and hydrophobic encapsulation for Si. Also, the films have a large effective area conferring them high optical absorption, which actively contribute to the solar energy harvesting together with Si. Here, we report photovoltaic devices with photoconversion efficiency up to 12% and a record 100% internal quantum efficiency (IQE). Such unprecedented IQE value is truly remarkable and indicates that every absorbed photon from the device, at some wavelengths, generates a pair of separated charge carriers, which are collected at the electrodes. The SWCNT/Si devices favor high and broadband carrier photogeneration; charge dissociation of ultra-fast hot excitons; transport of electrons through n-Si and high-mobility holes through the SWCNT percolative network. Moreover, by varying the film thickness, it is possible to tailor the physical properties of such a two-dimensional interacting system, therefore the overall device features. These results not only pave the way for low-cost, high-efficient, and broadband photovoltaics, but also are promising for the development of generic SWCNT-based optoelectronic applications.

1. Introduction

Third generation photovoltaics require a combination of low-cost and highly efficient materials in order to overcome balance-of-system costs. Carbon nanotubes (CNTs) are particularly attractive for their earth-abundant source materials, recently scalable fabrication [1], purification methods [2], and solution processability [3]. Moreover, the unique one-dimensional properties of CNTs allow the realization of solar cells that are highly thermally conductive and mechanical, chemical, and radiation resistant [4]. In particular, single-walled carbon nanotubes (SWCNTs) have suitable photophysical properties [4] for photovoltaics, such as high aspect ratio, direct subband gaps [5], and tunable photoabsorption from the near infrared (NIR) to the ultraviolet (UV) [2]. Notably, SWCNT electronic and optical subband gaps are in a wide range: from 0.5 to 5 eV. Generally, one of the criteria for obtaining the highest photoconversion efficiency (PCE) is the correct matching of the solar cell band gap to the solar spectrum. The optimal device band gap of 1.1 eV [6] can be easily obtained from 12–15 different nanotube chirality having the first optical subband gap between 1.0 and

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1.2 eV. Therefore, by using polychiral mixtures of both metallic and semiconducting SWCNTs it is possible having a broadband optical absorption in the UV-VIS-NIR range [7], harvesting in this way the majority of the solar photon flux, meanwhile avoiding the time-consuming sorting process required to isolate single-chirality distributions of SWCNTs [8]. Furthermore, the photogenerated carriers in SWCNTs are excitons with binding energies up to 0.4 eV at room temperature [9,10], which possibly may be multiple generated [11,12]. Consequently, such photogenerated excitons are ultra-fast transferred [13–15] through the SWCNT percolating network and they are dissociated into high-mobility (79000 cm^2/Vs) [16] free carriers in order to harvest their potential energy for solar cells and photodetectors. Such a dissociation is accomplished, for instance, by creating a heterojunction [17] with silicon (Si) due to the energetic band offsets greater than the SWCNT exciton binding energy [18]. In this way, charge generation, separation, transport, and collection can be realized partly by the semi-transparent, conductive SWCNT thin film and partly by Si. In addition, the large available surface area of the CNT random network films, provided by their multi-fractal hierarchical morphology [3], leads to strong and tunable optical absorption [7], anti-reflection [19] and an air-stable [20], hydrophobic encapsulation [3,21] for Si. For all these reasons, a deep understanding of polychiral SWCNT hierarchical random networks is critical in order to realize technologically relevant photovoltaic devices. Carbon nanotube/silicon (CNT/Si) heterojunction solar cells have steadily pushed the PCE up to 12% [22] without any post-process treatments, while up to 11% for chemically doped cells [23], 15% for integration with gold nanoparticles [8] or with anti-reflective coatings [24], and a record 17% [25] exploiting oxide layers. Despite these accomplishments, our fundamental understanding of the SWCNT/Si heterojunctions is still incomplete. Here, we report an unprecedented record 100% of internal quantum efficiency (IQE) for SWCNT/Si heterojunction solar cells. We also show for the first time that the multi-functional SWCNT film not only plays an active role in the heterojunction, but it also provides anti-reflection together with an air-stable and hydrophobic encapsulation for the solar cells. Furthermore, we introduce the SWCNT bulk heterojunction (BHJ), demonstrating that is a two-dimensional system formed by interacting SWCNTs. The optical and electrical properties of such a BHJ as well as those of the whole SWCNT/Si device are discussed. By independently optimizing the SWCNT film and Si thicknesses, we illustrate that it is possible to tailor in a controlled fashion the PCE of our solar cells up to 12±1%. Finally, we suggest a detailed model for the SWCNT/Si heterojunction.

2. Experimental

2.1. Realization of the SWCNT films

Highly pure single-walled carbon nanotube (SWCNT) powder (Sigma-Aldrich, CoMoCAT, assay 90%, no amorphous carbon, diameter: 0.7–1 nm) was dispersed in an aqueous solution (30 $\mu g\ mL^{-1}$) with 2% w/v sodium dodecyl sulfate (Sigma-Aldrich, assay $>98.5\%$) anionic surfactant. In order to disperse the suspension, SWCNTs were tip-ultrasonicated (Branson S250A, 200 W, 20% power, 20 KHz) in an ice-bath for an hour and the unbundled supernatant was collected by a pipette. The result was a well-dispersed suspension that was stable for several months. Single-walled carbon nanotube films were fabricated by a vacuum-filtration process of volume aliquots of the dispersion on mixed cellulose ester filters (Pall GN6, 1″ in diameter, 0.45 μm pore diameter). Subsequently, rinsing in water and in a solution of ethanol, methanol, and water (15:15:70) to remove the surfactant was performed.

2.2. Device fabrication

The substrates, provided by Fondazione Bruno Kessler (FBK), are in a top-down configuration. Au/Cr ohmic (n^+-Si) back contact (150 nm) was evaporated on n-type crystalline Si (100) wafers ($\rho \approx 3–12\ \Omega$ cm, $N_D \approx 6 \cdot 10^{14}\ cm^{-3}$) 4″ in diameter, passivated by thermal SiO_2 (300 nm). The SiO_2 layer was patterned in two different ways by a lithographic process with a positive resist followed by a chemical etching in order to obtain a batch of devices with a 3×3 mm bare Si window delimited by SiO_2. Therefore, the device active area is 0.09 cm^2. The Si wafers were made of different thickness (54–200 μm) by engraving the crystal only underneath the active area. An Au/Cr front contact electrode frame (150 nm) was then evaporated on SiO_2 by masking the Si active area. Then, wafers were cut in squares 1×1 cm. Single-walled carbon nanotube films were cut and deposited by dry-transfer printing [3,20] both on HF-etched Si active windows and on Carlo Erba soda-lime glass slides for the optical and electrical characterization.

2.3. Sample characterization

Optical spectroscopy (Agilent Cary 5000 UV/VIS/NIR) in transmission and reflection at room temperature with unpolarized light was performed on SWCNT films deposited on glass and Si. We estimated the film thickness through the Beer-Lambert law [3,7]. The SWCNT microstructure was observed by FEG-SEM (Leo 1503). The acquired micrographs were analyzed by an image software. The XPS measurements were performed on the SWCNT films deposited on Si by a PHI 1257 ESCA apparatus working in ultra-high vacuum (UHV) at a pressure of $5 \cdot 10^{-10}$ Torr. The system was equipped with a PHI 04–548 dual anode X-ray source (Al/Mg anode), a PHI 10–360 hemispherical analyzer, and a PHI 06–110 scanning electron gun. Non-monochromatic Mg X-ray source ($h\nu = 1253.6$ eV) with resolution 0.8–1.0 eV was employed. Raman measurements were performed on SWCNT films deposited on Si by a LabRam high resolution Raman microscope (HORIBA Jobin Yvon) using a laser with an excitation wavelength $\lambda = 633$ nm. Electrical measurements were carried out by a Keithley 2602 A digital multimeter interfaced to a PC. Sheet resistance values were determined by van der Pauw method after measuring the electrical resistance at room temperature in standard four probe configuration. The same configuration was used to measure the electrical resistance as a function of the temperature in a He bath, fixing the samples at the tip end of a descendant in thermal contact with a Cernox thermometer. Solar cells were tested using a LOT-Oriel solar simulator under AM 1.5 G spectral illumination of 100 $mWcm^{-2}$ (1 sun). The output power density of the simulator was calibrated using a power meter. Our systematic error on the photoconversion efficiency and the fill factor is estimated by the standard deviation over five samples realized in the same way. This small uncertainty demonstrates the high reproducibility of our SWCNT/Si solar cells. External quantum efficiency was measured with a custom optical setup: a LOT-Oriel Xe lamp emits white light passing through an Applied PhotoPhysics 300–1000 nm monochromator controlled by PC. Emerging monochromatic light is focused by a lens and divided by a chopper into two beams refocused by two lenses. One beam is then detected by a Si photodiode and the other impinges on the SWCNT/Si solar cell. Both AC signals are matched by an Acquire 7265 lock-in connected to a PC. The diffuse reflectance spectra of the SWCNT/Si devices were obtained by using a combination of the Agilent Cary 5000 UV/VIS/NIR spectrometer and Agilent integrating sphere in double-beam mode at a fixed incident angle ($\theta = 0$). The total reflectance spectra were measured at a fixed incident angle ($\theta = 3^\circ 20''$), in order to collect also the specular reflectance of the samples. We characterized the wettability of SWCNT/Si solar cells,