Improved efficiency of smooth and aligned single walled carbon nanotube/silicon hybrid solar cells†

Xiaokai Li,‡ Yeonwoong Jung,‡ Kelsey Sakimoto,‡ Teng-Hooi Goh,‡ Mark A. Reed‡ and André D. Taylor*‡

Smooth and aligned single walled carbon nanotube (SWNT) thin films with improved optoelectronic performance are fabricated using a superacid slide casting method. Deposition of as made SWNT thin film on silicon (Si) together with post treatments result in SWNT/Si hybrid solar cells with unprecedented high fill factor of 73.8%, low ideality factor of 1.08 as well as overall dry cell power conversion efficiency of 11.5%.

Introduction

Carbon nanotubes (CNTs), especially single walled carbon nanotubes (SWNTs), have extraordinary properties such as high mobility (~10^5 cm^2 V^{-1} s^{-1}),^1 on-off current ratio (>10^8),^2 and current carrying capacity (>10^7 A cm^{-2}).^3 Recent improvements in synthesis,^4 large-scale single chirality separation,^5 and rapid solution processing and assembly techniques^6,7 further improves the viability and versatility of CNTs in energy storage and conversion devices. In fact, CNT has already been used to contact many emerging solar materials. In addition, studies that combine carbon nanotube with silicon, a well-characterized semiconductor, could provide valuable insight into how photo-generation, transport, and dissociation of excitons and charge carriers function in large ensembles of CNTs. Optimizing this interface could serve as a platform for many next generation solar cell devices including CNT/polymer, carbon/polymer, and all carbon solar cells.\(^\text{14−16}\)

A CNT/Si hybrid solar cell typically consists of an n-type (or p-type) single-crystalline silicon coated by a thin film of p-type\(^\text{17}\) (or n-type)\(^\text{18}\) CNTs. The transparent CNT film functions as a charge carrier collecting conductive electrode and establishes a built-in potential\(^\text{19}\) interfacing with Si, which separates photo-generated carriers to yield a photocurrent. p-CNT/n-Si hybrid solar cells have received more intensive study as CNTs naturally develop p-type characteristics when exposed to air.\(^\text{20}\) Toward designing high efficiency SWNT/Si photovoltaic devices, the systematic optimization of the materials, the optoelectronic/morphological properties of the SWNT films, and the SWNT/Si interfaces are essential.

Single-walled carbon nanotubes (SWNTs)\(^\text{21}\) present more advantages over doubled\(^\text{19,22}\) (or multi-\(^\text{23}\) walled carbon nanotubes owing to their tunable/direct band gap energies matching with a wide range of the solar spectrum and better charge carrier transport properties.\(^\text{7,18,14,24}\) For heterogeneous mixtures of metallic and semiconducting SWNT films, thinner and sparse films are desirable in terms of optical properties since light absorbed in the carbon nanotube layer does not contribute to the power conversion efficiency due to the presence of metallic nanotubes which rapidly quench excitons in their vicinity.\(^\text{16}\) Simultaneously, in terms of electrical properties, dense thick SWNT films are more favorable to allow a larger diffusion length of minority carriers over the thickness of the SWNT films via the percolated networks,\(^\text{25}\) to minimize series resistance,\(^\text{17}\) and to improve the effective p-SWNT/n-Si interfacial area.\(^\text{26}\)

—Department of Chemical & Environmental Engineering, Yale University, New Haven, Connecticut 06511, USA. E-mail: andre.taylor@yale.edu

—Department of Electrical Engineering, Yale University, New Haven, CT 06511, USA

—Department of Applied Physics, Yale University, New Haven, CT 06520, USA

† Electronic supplementary information (ESI) available: Microscope images, ideality factor calculation, sheet resistance and transmittance results, \(J-V\) characteristics in the semi-logarithmic scale at the forward linear region. See DOI: 10.1039/c2ee23716d
The successful fabrication and assembly of SWNT films with the aforementioned desired properties requires a special SWNT process that can maintain good control of the dispersed SWNTs. Current SWNT dispersion techniques are not ideal because chemical functionalization disrupts the electronic properties of the SWNTs\(^\text{27}\) and stabilization via polymers/surfactants introduces non-SWNT materials into the final product.\(^\text{28}\) Sonication, widely used in the SWNT process, is also not appropriate as it reduces the length of the SWNTs, and thus inhibits the formation of the SWNT percolation network.\(^\text{29}\) Recently, we demonstrated that SWNT films prepared by the Mayer rod coating method possess optoelectronic properties that compete with the best SWNT thin films fabricated by any other techniques so far.\(^\text{30}\) This superiority comes from the use of a non-covalent stabilizer, carboxymethyl cellulose (CMC), which disperses the SWNTs during the Mayer rod process. The subsequent removal of the CMC stabilizer after the film formation minimizes the contact resistance between the individual SWNTs and maintains the collective electronic properties of the SWNT network.

At the interface of SWNT/Si hybrid solar cells there are a great multitude of tiny nanotube–silicon junctions where SWNTs are in physical contact with the Si surface. Within the carbon nanotube network, many SWNTs overlap and suspend on each other without contacting the Si. As a result, the solar cell performance suffers as surface recombination takes place at the exposed bare Si surfaces.\(^\text{19,21}\) Wadhwa et al.\(^\text{31}\) introduced an ionic liquid electrolyte between the SWNT networks that induces a depletion layer in the silicon. The electric field accumulates holes at the surface and also repels electrons. Photogenerated holes can thus diffuse along the Si with reduced surface recombination prior to an encounter with a nanotube where they are collected. Jia et al.\(^\text{22}\) introduced the occupation of the bare Si surface between the porous SWNT network with nitric acid solution. The acid can induce an inversion layer in the device leading to an enhanced performance.\(^\text{22,32}\) We suggest a more effective approach could be to fabricate a highly smooth and dense SWNT network to maximize the effective p–n junction interface. Yet fulfilling this task without jeopardizing the transparency and conductivity of the SWNT network has been extremely challenging with few related advanced material approaches in the literature.

In this paper, we report the engineering of high-efficiency SWNT/Si solar cells by utilizing a sliding method on superacid dispersed SWNTs to create SWNT films with the following advantages for photovoltaic applications: (a) combination of high transparency and conductivity for improved light absorption and carrier transportation; (b) extremely low surface roughness for a seamless interface with Si for efficient carrier dissociation; (c) mechanical robustness with high flexibility and ease of fabrication/deposition. Here we show a systematic study on the performance of SWNT/Si solar cells using two distinct methods (Mayer rod and superacid slide casting methods) for fabrication of SWNT films. We also describe the effects of various post-fabrication methods (i.e. doping) on the solar cell performance, and present the device parameters of optimized solar cells. These SWNT/Si photovoltaic devices have a fill factor (FF) of 73.8%, ideality factor of 1.08 and efficiencies for dry cells up to 11.5%. For the wet cells, we suggest that the observed extraordinary high short circuit currents are due to light bending from the liquid on the surface of the hydrophobic SWNT thin films.

**Experiment procedure**

SWNT thin film fabrication methods: superacid slide coating method: 3 mL of chlorosulfonic acid (Fluka, purum 98%) is added to 14 mg of single walled carbon nanotube (SWNT) (kindly supplied by SouthWest NanoTechnologies) and stirred vigorously for 3 days, inside a glove box filled with nitrogen. A drop of the prepared SWNT ink is sandwiched between two glass slides. The slides are manually pressed together until the desired film thickness is achieved (typically 30 to 50 nm). The two slides are rapidly slid across each other in opposite directions, producing a SWNT film on each glass slide. Each slide is either dried slowly inside a glove box or gently dipped into deionized water to remove any acid leached out of the film. The resulting film is floated on the top of the deionized water allowing transfer to another substrate.

SWNT/Si device fabrication: 500 nm-thermal oxide covered n-type Si (100) wafer (1–10 Ω cm) are patterned with Au (80 nm: top contact and etch mask)/Cr (5 nm: adhesion layer) by photolithography. Si windows (3 × 3 mm\(^2\)) are exposed by the wet-etch of the oxide. The back contacts are fabricated using Cr/Au, or Al following a buffered oxide etch (BOE) for 1 min. The SWNT thin films are transferred onto patterned Si wafers by floating on water and then, picked up by the wafers.

**Results and discussion**

The SWNT films are fabricated by the superacid sliding method in the following steps. Briefly, the SWNTs are stirred in chlorosulfonic acid, which dissolves the SWNTs by reversibly protonating their walls. The Coulombic repulsion between the SWNTs facilitates disaggregation by counteracting the strong intertube van der Waals attractions.\(^\text{34}\) Several drops of this superacid dispersion are sandwiched between two glass slides where they are spread and sheared (Fig. 1a). The film thickness is controlled by the dispersion amount and the force applied to spread the solution into a thin film. As-made films can then be coagulated using deionized water, or slowly dried in anhydrous air.

We show that SWNT films prepared by the superacid sliding method are consistently more transparent than the Mayer rod SWNT films of the same sheet resistance (Fig. 1b). To assess the optoelectronic performance of SWNT network films, we use a figure-of-merit based on the ratio of the direct current conductivity, \(\sigma_{dc}\), to the optical conductivity, \(\sigma_{ac}\) (typically at 550 nm).\(^\text{35}\) A higher value of \(\sigma_{dc}/\sigma_{ac}\) indicates a better photovoltaic film and the superacid SWNT films exhibit a \(\sigma_{dc}/\sigma_{ac}\) value of 11.2, while that for the Mayer rod SWNT films is 6.48. This huge improvement is attributed in part due to the formation of a better SWNT dispersion from superacid solution. Davis et al.\(^\text{34}\) presented Cryo-transmission electron microscopy of SWNTs in
chlorosulphonic acid with individual SWNTs forming an isotropic concentrated phase. In our superacid casted films, we observed a small bundle size of \( \sim 4 \text{ nm} \) (Fig. 1c). The improvement is also due to the avoidance of sonication (required for the Mayer Rod) in the dispersion process. The superacid method gently disperses the SWNTs using magnetic bars and hence preserves the integrity and length of the carbon nanotubes. Surprisingly, the SWNT films prepared by the superacid sliding method present better mechanical robustness/uniformity and ease of handling. In both the superacid and the Mayer rod coating process, the SWNTs are first coated on glass slides and subsequently transferred onto the Si wafer through a water-floating process. The structural integrity of the SWNT films on water facilitates the transfer process, which directly influences the SWNT/Si interfacial quality and solar cell performance. The Mayer rod SWNT films on water tend to wrinkle and disassemble (especially for thin films with high transmittance \( \sim 85\% \)); hence, disturbing the structural uniformity during the transfer step. Meanwhile, the superacid films are extraordinarily robust and retain their integrity during transfer even when they are extremely thin (\( \sim 8 \) to 10 nm thickness corresponding to \( \sim 95\% \) transparency at 550 nm wavelength). We attribute this robustness to the formation of highly aligned and woven networks of SWNTs induced by the shear forces involved in the sliding steps during the superacid process. We show that the SWNT bundles that are thicker than \( \sim 15 \text{ nm} \) are highly aligned along the shearing direction and form a spinal structure while thin bundles smaller than \( \sim 10 \text{ nm} \) randomly binds the aligned spines forming strong and woven networks (Fig. 1c).

We note that the surfaces of the superacid films are smoother than our previously designed Mayer rod films which represent the best in class with an surface root-mean-square (RMS) roughness of 11.2 nm.\(^{39}\) Since the bottom side (in contact with a glass slide) of the superacid casted film is interfaceted with the surface of a Si wafer in SWNT/Si devices, the roughness of the bottom surface is more critical for maximizing the p–n junction areas. Remarkably, the slowly dried superacid casted films have a RMS 2.78 nm (Fig. 1d). To the best of our knowledge, these slowly dried superacid films are the smoothest SWNT percolated thin films (with or without polymer filling the pores of SWNTs) that have been reported. We show in ESI† the importance of coagulation process in engineering the smoothness of superacid casted films. The RMS of the top surface for slowly dried films and water quenched films are 4.12 nm and 9.99 nm, respectively. (Fig. S1c and d)

We compare the performances of the SWNT/Si solar cells with the SWNT films prepared by the Mayer rod (Fig. 2a) and superacid slide casting method (Fig. 2b). We apply of 1% HF for 1 min onto SWNT/Si windows to improve the performances of all the devices owing to the removal of native oxides and H-passivated Si surfaces (Fig. S2†). These devices are called “as made” devices.

We further treated the as made cells with a nitric acid (\( \text{HNO}_3, 0.5 \text{ mol L}^{-1} \)) solution to further p-dope the SWNTs.\(^{37}\) Enhanced p-doping of SWNT is expected to result in a larger \( V_{oc} \) by increasing the built-in electric field at the SWNT/Si interface and improves the separation efficiency of the photo-generated carriers. Every device has three states in this study: state one, pretreatment (as made); state two, with wet nitric acid; state three: nitric acid treated and dried. Superacid SWNT/Si devices consistently behave better at all three states. In Table 1, we summarize the performance of Mayer rod SWNT/Si and superacid SWNT/Si devices when nitric acid dries (state three). It is noteworthy that superacid method yields better performance in all aspects of the devices, including lower ideality factor, higher \( V_{oc} \), Fill Factor (FF) and power conversion efficiency (PCE). While this improved performance partially results from the difference in optoelectronic performance (Fig. 1b), it is also
attributed to the improved smoothness of superacid SWNT films as compared to that of Mayer rod SWNT films. Surface roughness controls the effective interfacial area between SWNT network and Si, which determines the distance minority carriers need to travel along the Si surfaces to be dissociated and get collected. Smaller distance is of vital importance to facilitate carrier dissociation and to minimize surface recombination so that lower ideality factor and higher FF can be achieved. Data in Fig. 2c and d are extracted from AFM images.

**Table 1** Device performance of Mayer rod SWNT/Si and superacid SWNT/Si devices after nitric acid dries

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ideality factor</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mayer rod SWNT/Si</td>
<td>1.41</td>
<td>0.50</td>
<td>22.03</td>
<td>0.47</td>
<td>5.14</td>
</tr>
<tr>
<td>Superacid SWNT/Si</td>
<td>1.13</td>
<td>0.51</td>
<td>26.11</td>
<td>0.64</td>
<td>8.52</td>
</tr>
</tbody>
</table>
of Mayer rod and superacid SWNT films. Fig. 2c demonstrates a much smoother surface from superacid than Mayer rod made SWNT films. It also defines the concepts of “baseline” and “depth” used in Fig. 2d. Using the tallest point of the original AFM image as a baseline, Fig. 2d shows the ratio the projected SWNT network area on Si to the Si geometry area as a function of depth. This ratio represents the percentage of SWNT in contact with Si if the SWNT network of the corresponding depth were flattened. It is obvious that the bigger the percentage within a small depth, the larger the effective SWNT/Si interfacial areas are. The smoothness of superacid SWNT films renders a greatly enhanced contact between SWNT and Si (Fig. 2d). Fig. 2e and f visualize the effective contact area and not in contact area assuming that the highest 16% of the SWNTs plus a 1.5 nm area assuming that the highest 16% of the SWNTs plus a 1.5 nm (SWNT diameter) can be in contact with the Si. A depth of 37.88 nm and 117.46 nm are used for the superacid and the Mayer rod SWNT films respectively. The carriers generated at Si surface need to travel on average 14.6 nm and 55.5 nm to reach the nearest SWNT/Si interface for the superacid coated and the Mayer rod coated SWNT thin films, respectively. When a depth of 37.88 nm is used for Mayer rod SWNT devices (Fig. S3†), an average distance of 2.2 μm is needed. The actual depth depends on the flexibility and deformability of SWNTs thin films. These estimates indicate that, statistically, excited carriers need to travel for a shorter distance along the Si surface to reach SWNT/ Si interfaces in superacid devices than that in Mayer rod devices.

Upon nitric acid treatment, the following three phenomena are also observed (Fig. 2a and b): (1) for both films, the devices treated with HNO₃ (both state two and three) show improved performances compared to pretreatment devices (state one); (2) the efficiency when nitric acid solution is present (ηₑₓₑₚ; state two) is higher than efficiency when nitric acid film is added and dried (ηₑₓₑₓ; state three) with ηₑₓₑₓ/ηₑₓₑₓ = 1.32 for superacid films. Yet for Mayer rod films it is the reverse (ηₑₓₑₓ/ηₑₓₑₓ = 0.55). The efficiency increase for superacid devices are mainly due to improved Jₑₓₑ, while the efficiency decrease for the Mayer rod is a result of a reduced FF and Vₑₓₑ; (3) the Jₑₓₑ (state two) is consistently larger than the Jₑₓₑ (state three) with Jₑₓₑ/Jₑₓₑ of 1.33 and 1.08 for superacid and Mayer rod SWNT films, respectively.

Jia et al. attributed the larger Jₑₓₑ in the wet state over the dry state to a photoelectrochemical reaction.23 Studies by D. Michalak and N. Lewis32,33 demonstrate that the aqueous acidic electrolyte can induce an inversion layer, reducing the surface recombination velocity. The observed increase in solar cell performance is more likely due to this effect. Besides, the intermediate index of refraction of acidic electrolyte relative to air and Si leads to reduction in light reflection, which also contributes to a larger Jₑₓₑ (Fig. S4†). In addition, the SWNT fabrication dependence with nitric acid treatment implies that certain surface properties of SWNTs controlled by the SWNT preparation method changes the way the SWNTs interface with the nitric acid solution and determines the solar cell characteristics.

We suggest that the wetting nature of SWNT thin films correlates with these observations and present the contact angle measurements of HNO₃ droplets on the SWNT films. Large contact angles of 98° (Fig. 2b inset) are observed from the SWNT films prepared by the superacid methods, revealing the hydrophobic nature of these samples. Meanwhile, 37° is shown for the Mayer rod prepared SWNT films (Fig. 2a inset). We hypothesize that the enhanced efficiencies of SWNT/Si devices in their wet states come from a “light concentration effect” owing to the hemispherical droplets that efficiently incouple the incident light.34 Since the superacid SWNTs are hydrophobic, the sharper curvature of the droplet leads to a stronger light concentrating effect and higher Jₑₓₑ enhancement. In contrast, a flat droplet on a hydrophilic film (via the Mayer rod method) results in a lower concentration effect and hence a smaller Jₑₓₑ enhancement. In addition, hydrophilic films tend to delaminate and float on nitric acid solution, deteriorating the carrier dissociation at the SWNT/Si interface and leading to a lower FF and Vₑₓₑ as shown with Mayer rod made films (Fig. 2a).

**Fig. 3** (a) Variation of Jₑₓₑ with multiple cycles of with/without of water droplet on the surface of a hydrophobic SWNT/Si solar cell. (b) J–V characteristics of a Mayer rod SWNT/Si solar cell under 0.1 sun of solar simulation before (top curve) and after (bottom curve) incorporating a light concentric effect from water droplet place on top of a hydrophobic glass.
To verify the proposed light concentration effect and isolate other possible contributions, we applied a droplet of deionized water onto the SWNT/Si window of a cell with a hydrophobic SWNT network, and characterized the performance before/after the water droplet dries. We show that the $J_{sc}$ consistently increases with the addition of a water droplet and recovers to the original low values when it dries, in multiple cycles between the wet and dry states (Fig. 3a). By optimizing the size (coverage of the p–n junction area) of the water droplet, we report that the $J_{sc}$ can be increased up to $\sim$1.9 times over the dry state with hydrophobic cells. An image of water droplet in a hemispherical shape on an operating cell is shown in Fig. S5.† As a control experiment, we placed a water droplet onto a hydrophobic-coated glass placed on the top of a hydrophilic Mayer rod cell under illumination and show a $\sim$2.8 times increase in $J_{sc}$ (at 0.1 sun of solar simulation (10 mW cm$^{-2}$)) compared to without the water droplet (Fig. 3b). A maximum power generation of 0.87 mW cm$^{-2}$ is obtained demonstrating an efficiency of 8.7% before applying a water droplet. In the presence of the water droplet, a maximum power generation as high as 2.7 mW cm$^{-2}$ (defined using SWNT/Si device area) is obtained which corresponds to a $\sim$3.1 times increase in power output. This result suggests that the light concentrating effect from the nitric acid due to the hydrophobicity of the SWNTs is the major contributor to the observed enhanced $J_{sc}$ instead of the photo-electrochemical reaction.

We further investigate the intrinsic p-doping effect of SWNTs using gold salt; gold salt is known to be reduced on the surface of CNTs, thus, providing a p-doping effect.39 We treated the superacid cells with various concentrations of AuCl$_3$ salt in nitromethane, and compare their performance in the dry states, ruling out the light concentration effect. We observe 1.2–1.3 times $J_{sc}$ increases with the addition of AuCl$_3$ solution (2 mM to 10 mM) in all the tested range of solar intensity (0.1 sun to 1 sun) (Fig. 4a). This is partially due to a slight (3%) increase in transmittance due to the depletion of the second singularity (filled electronic states),40 which results in the loss of the corresponding electronic transition and loss of the associated S$_2$ absorption intensity (Fig. S6†). Transmission electron microscopy (TEM) characterization on the side of the SWNT film (super-acid sliding) in contact with the Si wafer after 10 mM gold salt treatment (Fig. 4a bottom inset) reveals a large number of nanoparticles ranging in size from $\sim$1 to 2 nm to $\sim$100 nm with single-crystalline structures (lattice fringes in Fig. 4a bottom inset) as also confirmed by energy-dispersive X-ray spectroscopy elemental mapping (Fig S7†). The presence of gold (Au) nanoparticles suggests that optical scattering from these nanoparticles is also likely to participate in enhancing the light

![Fig. 4](a)–(d) Solar intensity-dependent variation of device parameters in superacid SWNT/Si solar cells with varying AuCl$_3$ concentration. (a) $J_{sc}$, and normalized $J_{sc}$ over pre-Au doping in the upper inset. Lower inset shows TEM micrographs of a SWNT film prepared with a AuCl$_3$ of 10 mM (b) $V_{oc}$. (c) FF. (d) Efficiency.

Energy Environ. Sci. This journal is © The Royal Society of Chemistry 2013
absorption. We therefore believe the observed enhancement of $J_{sc}$ is most likely a combination of both effects. We found that the $J_{sc}$ decreases at 10 mM (compared to 5 mM) of AuCl$_3$ and observed a huge degradation in device performance when doped with 20 mM AuCl$_3$. We attribute this observation to a “shorting” problem as an excess amount of Au nanoparticles form an intimate contact with the Si. The local Si–Au–SWNT junctions could disrupt the p–n junction areas.

We reveal that the $V_{oc}$ increases with increasing AuCl$_3$ concentration up to 10 mM and decrease at higher concentrations (Fig. 4b). The increase of $V_{oc}$ with Au doping can be explained by the increase of charge carrier density of SWNTs. The p–n junction solar cells made of thin p-type emitter (SWNT in our case) on n-type Si wafer, $V_{oc}$ is given by

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{\Delta p(N_n + \Delta n)}{n^2} + 1 \right)$$

where $k$, $T$, $q$, $n$, $N_n$ represents the Boltzmann constant, temperature, unit charge, intrinsic carrier concentration of Si, and n-doping concentration, respectively. Since, $\Delta p$ ($\Delta n$) represents the excess minority carriers (holes and electrons, respectively) imposed by doping, the equation predicts a higher $V_{oc}$ with increased p-doping of the SWNT. In our device geometry, the SWNTs functions as both a donor and as a transparent conductive electrode. The increase of $V_{oc}$ with increased work function of the transparent conductive oxide front contact electrode was observed in amorphous Si/crystalline-Si hetero-junction solar cells where the thin amorphous Si functions as an emitter. The above equation is also expressed as:

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{J_{sc}}{J_0} \right)$$

where $J_0$ is the saturation current density. From dark $\ln(J)-V$ plots, $J_0$ is determined by extrapolating the linear slope of $\ln(J)-V$ to zero bias and $J_0$ is found to decrease with increasing Au concentration; $J_0^{5\text{mM}} = 3.68 \times 10^{-6}$ mA cm$^{-2}$, $J_0^{20\text{mM}} = 2.78 \times 10^{-6}$ mA cm$^{-2}$, $J_0^{50\text{mM}} = 2.26 \times 10^{-6}$ mA cm$^{-2}$ (Fig. S8). The decrease of $J_0$ and the increase of $J_{sc}$ together also predict the increase of $V_{sc}$, consistent with our observation.

The fill factor, FF, is also observed to increase with increasing AuCl$_3$ concentration (Fig. 4c). This is primarily due to the reduction of SWNT thin film sheet resistance (Fig. S9). This improvement results in an increase of the overall efficiency (Fig. 4d); 1.7 times increase at 1 sun (from 5.3% to 9.13%) and 1.5 times increase at 0.1 sun (from 7.2% to 10.8%) with 5 mM Au doping over un-doped cells.

Fig. 5a shows the $J-V$ characteristics of the optimized superacid SWNT/Si solar cells both in dark (inset) and under illumination. We use Al as the back contact (Fig. S10†) and chromium/gold (Cr/Au) as the front contact. The SWNT thin films are casted by our superacid sliding method and slowly dried in anhydrous air. The films are transferred on pre-patterned Si wafers that are freshly treated by HF. The cells are then treated subsequently with a 0.5 mol L$^{-1}$ nitric acid and a 5 mM gold salt solution by spin casting. The inset shows the dark $\ln(J)-V$ characteristics which yields an ideality factor of 1.08. At 1 sun, $V_{oc}$ of 0.533 V, $J_{sc}$ of 29.31 mA cm$^{-2}$ and FF of 73.8% are obtained, resulting in a power conversion efficiency of 11.5%. Another important feature of our optimized solar cell is its long minority carrier lifetime characterized by the reverse recovery transient method. This characterization method relies on the transient dynamics of carriers electrically injected into the depletion layer of p–n junctions. A p–n junction diode is subject to an abrupt switching of the forward-to-reverse bias, resulting in a transient response from which the carrier lifetime is extracted. We show a reverse recovery transient characteristic (Fig. 5b) from the SWNT/Si solar cell in Fig. 5a. The corresponding current response shows three distinct phases of constant forward current ($I_0$), constant reverse current ($I_r$) and a constant storage time ($t_s$) followed by slow decay/saturation of the reverse current. The minority carrier lifetime is given by $\tau = t_s/\ln(1 + I_r/I_0)$, and is determined to be $\sim 35$ µs in dark, which is comparable (5.9 to 19.3 µs) to the lifetimes of high-quality, poly crystalline p–n junction Si solar cells grown/processed at high temperatures.

![Fig. 5](image-url) (a) $J-V$ characteristics showing 11.5% efficiency under 1 sun from an optimized cell. (b) Reveres recovery transient characteristic from an optimized cell. All the data from (a) and (b) were obtained from superacid SWNT/Si cells.
small ideality factor close to unity suggests that the observed dark $J$–$V$ characteristics were not severely affected by carrier recombination at the interfaces of SWNT/Si. These findings suggest that the photovoltaic efficiency may be further improved by enhancing the absorption/trapping efficiency of the incoming light by patterning Si and increasing the interfacial area of SWNT/Si, which is currently under investigation.

Conclusions

We present improved SWNT/Si solar cells by applying advanced SWNT film preparation methods and post-fabrication treatments. We show the superior performance of solar cells prepared by the superacid sliding method, which benefits from the superior optoelectronic properties, morphological uniformity and robustness of the SWNT films. By optimizing the SWNT material properties as well as the SWNT/Si and metal interfaces, we greatly improved the $J_{sc}$, $V_{oc}$, and FF, and achieved a maximum efficiency of 11.5% at 1 sun. We also identified that the CNT wettability significantly affects solar cell characteristics in their wet state and unveiled that the increased short circuit current reflects the reduced recombination at the interfaces of SWNT/Si. These findings were not severely affected by carrier recombination at the interfaces of SWNT/Si. These findings suggest that the photovoltaic efficiency may be further improved by enhancing the absorption/trapping efficiency of the incoming light by patterning Si and increasing the interfacial area of SWNT/Si, which is currently under investigation.

Acknowledgements

This work was supported by the SOLAR program of the National Science Foundation under DMR-0934520. Support is also acknowledged from the NSF-CAREER award (CBET-0954985) and NASA (CT Space Grant Consortium). Support is also acknowledged by ‘Nanostuctures for Electrical Energy Storage’, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award number DESC0001160 (Y. J. and M. A. R.). The authors acknowledge Dr Nilay Hazari for helpful discussions, for allowing us to use his facilities as well as his help with superacid preparation and processing. Southwest Nanotechnologies are acknowledged for their kind supply of single walled carbon nanotubes. David Kohn is acknowledged for helpful discussion. Facilities use was supported by YINQE and NSF MRSEC DMR 1119826.

Notes and references