

## Carbon Nanotubes - Si Hybrid Solar Cells

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This short review describes recent results in the field of carbon nanotube (CNT) – Si hybrid photovoltaics (PV) focusing on advantages of semiconducting carbon nanotubes over other organic materials used in organic- Si composite photosensing materials. Possible mechanisms of charge photogeneration at CNT- Si interface and charge transport are discussed. Perspectives and future trends in research of this novel class of PV nanohybrids are presented as well.

**Keywords:** Carbon nanotubes, Silicon, Solar cells, Nanohybrids.

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### 1. INTRODUCTION

Silicon remains the dominant material in photovoltaic industry due to excellent optoelectronic properties, stability and its sufficient supply in the environment. Today, silicon based solar cells occupy more than 80 % of the commercial photovoltaic market. However, the further broad dissemination of Si PVs is partially limited by an expensive price of high quality crystalline Si wafers as well as the complicated fabrication process. The use of nanotechnology and employment of novel organic materials in combination with inexpensive polycrystalline, amorphous Si either nanostructured Si such as porous Si (PSi) or Si nanowires (SiNW) opens an opportunity to develop a new generation of hybrid organic/Si solar cells with a conversion efficiency higher than 10% and a fabrication cost lower than for conventional Si PV technologies. For the past several years, there was a surge of research dealing with the investigation of photosensitive hybrid materials comprising Si nanostructures (SiNW array [1-3], free standing Si NW[4-6], porous Si [7-10]) interfaced with polymers, oligomers and small molecules. Also, there have been substantial research efforts devoted to the investigation of organic/crystalline Si heterojunctions [11]. Nevertheless, in terms of PV performance, conjugated polymers have serious drawback as compared to their silicon counterpart due to gradual degradation, photobleaching and low charge mobility making the further progress challenging, firstly because of poor long term stability.

In this context, carbon nanotubes (CNTs) present an almost ideal organic compound to be interfaced with Si to create an efficient light harvesting nanohybrid structure. Specifically for CNT/Si hybrid solar cells, several advantages over other organic materials may include: high charge mobility, size dependent band-gap, efficient absorbance in NIR spectral range for semiconducting single walled carbon nanotubes (s-SWNT) ; simple doping by acid treatment allowing significantly reduced film resistance thin CNT film can simultaneously work not only as a photoactive material, but also as a transparent conductive electrode, replacing con-

ventional metal grids or metal oxide coatings (for other organic materials a deposition of the top metal/metal oxide electrode is required); Fermi level of s-SWNTs can be shifted through either the electrical or chemical doping and functionalization resulting in a favorable position to increase built-in electric field at the interface with silicon.

### 2. SWNT – CRYSTALLINE SI SOLARS

Recently a photoconversion efficiency record of 13.8% has been reported for SWNT/Si solar cells [12] exceeding the best PCEs for any organic (8-10%) and DSSC (10-12%) devices. Such remarkable results were achieved for a relatively short term (about five year since first report in 2007 with PCE of ~ 1% for similar device [13]) suggesting further progress in the nearest future. Such high efficiency can be associated with several factors. First, the use of high quality *p*-type semiconducting SWNT forming *p-n* heterojunction with *n*-type Si. It means that s-SWNTs contribute to not only charge separation and transport, but also to NIR light absorbance; Second, SWNT doping by dilute HNO<sub>3</sub> reduces SWNT film resistance (and consequently device serial resistance) resulting in an increase of fill factor and short circuit current; Third, SWNT infiltration with the acid results in formation of Si-acid-CNT micro-units working as photoelectrochemical solar cells with acid as an aqueous electrolyte. Thus, two photosensitive mechanisms act in parallel: electrochemical and charge separation at *p-n* heterojunction. Also, SWNT film was encapsulated by polydimethylsiloxane (PMDS) to provide anti-reflection properties.

The doping of SWNT film by thionyl chloride also enhanced conversion efficiency more than 50% (PCE ~ 4% was achieved after doping) [14]. Using Hall-effect measurements, the change of the 2D carrier density and effective mobilities have been determined for undoped and doped SWNT film:  $3.1 \times 10^{15}$  vs  $4.6 \times 10^{17} \text{cm}^{-2}$ , and  $2.1$  vs  $17.2 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively. If increase of the carrier density after doping is expectable (an increase of hole concentration owing to oxidation), the mobility enhancement is not a trivial outcome and can be relat-

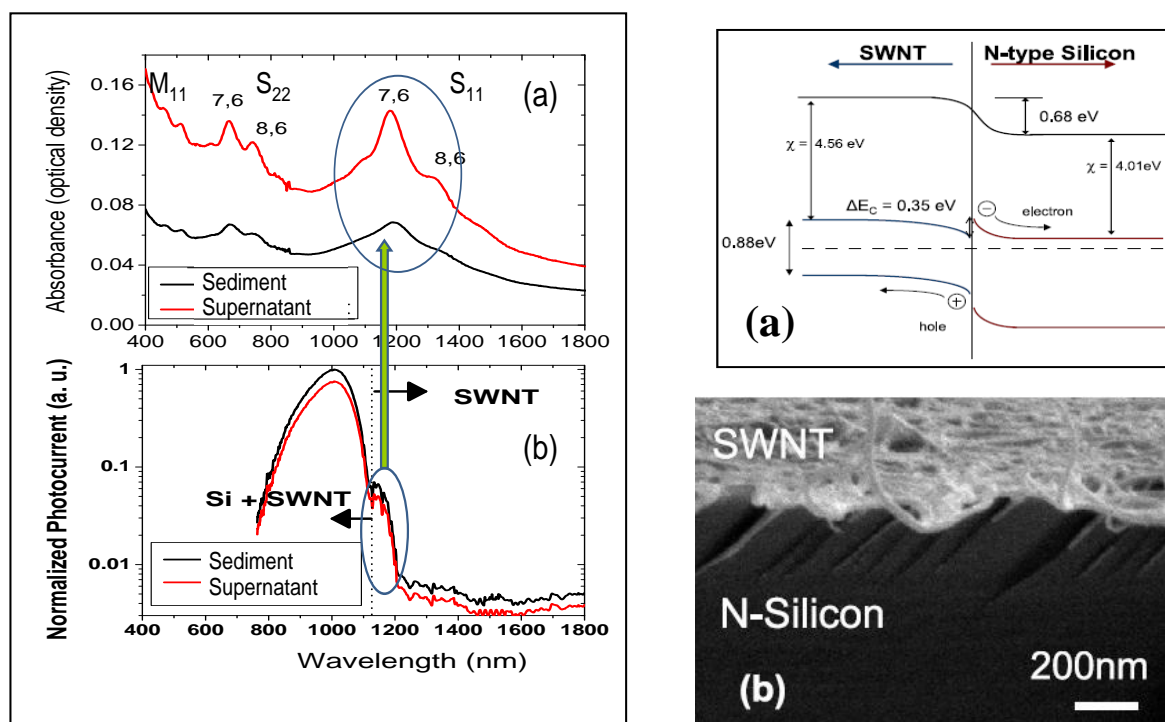
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ed to resistivity reduction at junctions between nanotube bundles and the lowering of barriers between s-SWNTs and m-SWNTs [14]. In spite of impressive progress in the study of optoelectronic properties of interface between carbon nanotubes and silicon, a lot of fundamental aspects of photoconversion at CNT/Si heterojunction require further investigation. For example, what is the role of the interface in dissociation of excitons generated in carbon nanotubes and photocarrier recombination process?; What junction type (Schottky diode or  $p-n$  diode) is formed between Si and SWNT film, where 1/3 of nanotubes are metallic and other 2/3 are semiconducting?; How Anderson model should be adjusted to quasi-1D nanotubes and their inhomogeneous density in the contact area with silicon (because of the high film porosity); What is the mechanism of the hole transport through the nanotube bundles and their junctions in the depletion region?

Ural et al [15] fabricated CNT/Si/Me planar structure to investigate the nature of contact between carbon nanotubes and silicon. It was found that thin CNT film forms Schottky contact with Si (both  $n$ - and  $p$ -type) and thermionic emission is a dominant transport mechanism above 240K, while for lower temperatures the major mechanism is tunneling. These results were consistent with metallic behavior of CNT film obtained from temperature dependency of resistivity, that could be associated with prevailing metallic nanotubes over semiconducting in the CNT network. While, other reports [14, 16,17] indicate  $p-n$  heterojunction between semiconducting SWNTs and  $n$ -type Si. An effect of elec-

trical gating on photoconversion process of SWNT/ $n$ -Si device has been exploited by Rinzler's group in recent reports [18,19]. The gating of SWNT film was performed in lateral geometry through electrolyte and SWNT film (gate electrode) insulated from the other SWNT film forming the Schottky contact with  $n$ -type Si. Upon negative bias of -0.75 V, PCE = 10.9% has been attained that demonstrated significant improvement compared to zero bias (PCE = 8.4%). Authors believe that such gate voltage- induced behavior can be explained by several mechanisms including (i) the enhancement of built-in potential owing to the shift of Fermi level, (ii) reduction of SWNT film resistivity; (iii) existence of the interface dipoles; and (iv) an appearance of additional electric field across the depletion layer in the  $n$ -Si [18].

So far, in all aforementioned studies, CNT/ $n$ -Si interface was considered as a Schottky photodiode [15,18,19] or as a  $p-n$  heterojunction [12-14]; however, without direct evidence of SWNTs (or DWNTs) contribution in light absorption, especially in the NIR range. Recent reports [16,17] clearly indicated the importance of semiconducting SWNTs as NIR light absorbing material with energies below Si band gap (1.1eV). Ong et al. [16] observed matching of the S<sub>11</sub> band (corresponding to the first interband transition for s-SWNTs with 7,6 and 8,6 chirality) with the photocurrent band located at ~1150 nm (Fig. 1, left). Thus, semiconducting SWNT network contributes to the photo conversion process not only as a charge separator/transporter/collector but also as a light absorber. This is an important fact,



**Fig. 1** – Left (a) UV-Vis-NIR spectrum of sediment and supernatant fraction from centrifugation process of SWNT films on glass. M<sub>11</sub>, S<sub>22</sub>, and S<sub>11</sub> represents the band-gap transitions in metallic and semiconducting SWNTs; (b) Normalized photocurrent spectra of the SWNT/ $n$ -Si solar cell devices (supernatant and sediment) showing a current band matching the S<sub>11</sub> absorbance band. Right (a) Schematic energy band diagram of SWNT/ $n$ -Si heterojunction based on the Anderson model. Electron affinity,  $\chi$ , and conduction band offset,  $\Delta E_c$ , for SWNT and  $n$ -Si are shown in the energy band diagram; (b) SEM images of cross-sectional view of SWNT/ $n$ -Si interface [16]

distinguishing between a *p-n* heterojunction solar cell with two active light absorbing components and a Schottky cell, where the metal component is not capable of absorbing photons. It was suggested that photo-generated excitons in SWNT dissociate to holes and electrons at the heterojunction followed by hole transport and collection through the SWNT network (Fig.1, right, a). In parallel, photoelectrons generated at the Si side diffuse from the depletion region to the external electrode. Also, photoholes from Si and photoelectrons from SWNT can be involved in charge separation process; however, with lower efficiency [16].

Hatakeyama et al. [17] also demonstrated a critical role of SWNTs as NIR photon absorbers for the enhancement of PV performance in the infrared spectral range. They compared conversion efficiency of SWNT/Si cell with the control sample (Ag/Si Schottky cell) observing a significantly higher PCE of SWNT based device for wavelengths longer than 850 nm. Additionally, they found that the encapsulation of C<sub>60</sub> inside nanotubes improve the device PV performance through adjusting the Fermi level of SWNTs. A similar contribution of carbon nanotubes in external conversion efficiency, however, for UV spectral range owing to  $\pi$ - $\pi$  plasmon band has been observed in study [20].

### 3. SWNT- AMORPHOUS AND NANOSTRUCTURED SI

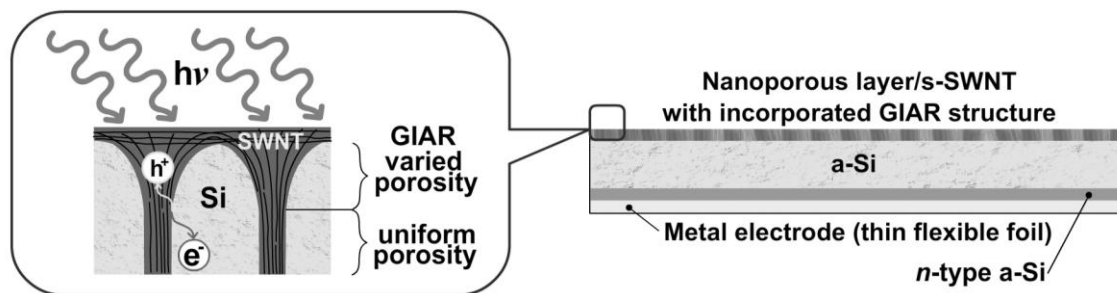
Another recent trend in the development of CNT/semiconductor light harvesting devices is the employment of amorphous Si [21-22] and nanostructured Si [23-25]. Hydrogenated amorphous silicon (a-Si) have advantageous over crystalline Si because of the lower cost and opportunity to fabricate thin film flexible structures comprising *p-i-n* junction ; however, the major drawback of a-Si is the low charge mobility. Nevertheless, today a-Si solars attract growing interest as a light weigh, thin film, flexible and cost effective alternative to crystalline silicon photovoltaics. The research of CNT/a-Si hybrids is now in the beginning stage; however, recent studies already see that there is promising potential for future PV applications. Schriver et al. [21] examined the photoactive properties of MWNT networks in junction with a-Si undoped thin film. The heterojunction demonstrated rectifying behavior and PV action with small short circuit current ( $\sim 0.25$  mA/cm<sup>2</sup>) that can be associated with the use of MWNTs (instead of s-SWNTs) and undoped a-Si (instead of *n*-doped Si). Interestingly, a similar device (with graphene layer instead of MWNTs) results in worse PV performance. A sophisticated design of coaxial solar cells has been reported by Zhou et al. [23] where heterojunction was constructed from a metallic inner core (MWNTs) contacting with the outer shell (a-Si). This strategy was based on coating vertically aligned MWNT nanowire (NW) array grown on the flat substrate with amorphous silicon shells followed by ITO deposition as a top contact. The short circuit current of coaxial MWNT/a-Si array showed a 25% increase in short circuit current without a noticeable change of the open circuit as compared with control sample – similar device with planar MWNT/a-Si heterojunction. These results suggested that coaxial solar cell works as a

manifold of individual freestanding photovoltaic nanowires (Schottky photodiodes) connected in parallel. An enhancement in PV performance has been explained not only by an increase of the interfacial area through the use MWNT NW array but also by the light trapping which is typical for many photovoltaics with nano/microstructured surfaces. Because MWNTs exhibit a low Vis-NIR extinction coefficient, the primary absorber was only a-Si, and thus potential of carbon nanotubes as Vis/NIR absorbers (such as s-SWNTs) was not utilized in this design [23]. The above circumstance gives a hint to employ semiconducting SWNTs interfaced with nanostructured silicon to further enhance light harvesting for such hybrid structures.

When s-SWNTs serve as effective light absorbers, an existence of nanostructured heterojunction with Si becomes critically important. Generally, the concept of nanostructured heterojunction is very beneficial for organic/inorganic interfaces with photoactive organic material, first of all, because of the relatively short exciton diffusion lengths in the organic component (e.g. 100-300 nm for SWNT and  $\sim 10$  nm for many conjugated polymers).

### 4. OUTLOOK AND FUTURE PROSPECTS

In spite of high expectations, CNT/SiNW array structure probably cannot satisfy the growing demand of PV community to thin film, flexibility and light weight features because crystalline Si is required for SiNW array preparation. In this context, it could be very beneficial to create a thin film, flexible solar device comprising amorphous Si forming nanostructured heterojunction (Fig.2) with semiconducting SWNTs. Such a solution can be realized through the direct growth of s-SWNTs inside the nanopores of etched a-Si film. Figure 2 shows the design of such a hypothetical solar cell that has a good chance to outperform existing thin film photovoltaics based on amorphous Si. Here, nanostructured heterojunction between *p*-type s-SWNTs and *intrinsic* nanoporous a-Si should provide important advantages over traditional *p-i-n* a-Si device: (i) The replacement of *p*-type a-Si by s-SWNTs will extend the device absorption range up to 2  $\mu$ m (instead of 0.73  $\mu$ m, limited by a-Si band gap) owing to s-SWNT absorbance of NIR light; (ii) Enhanced interfacial area between nanoporous *intrinsic* a-Si and s-SWNTs (200-800 m<sup>2</sup>/cm<sup>3</sup>) compared to the planar junction between *p*-type, *intrinsic*, and *n*-type a-Si; (iii) Higher carrier mobility for quasi- aligned nanotubes (up to 10<sup>5</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for individual nanotubes and  $\sim 60$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for SWNT films) as compared with a-Si (hole mobility is  $\sim 0.2$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and electron mobility is  $\sim 2$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>). Furthermore, because of controllable s-SWNT growth hole mobility can be even enhanced as compared with disordered nanotube network; (iv) Possibility to increase charge concentration and Fermi level tuning for s-SWNT by simple acidic doping or various functionalization; (v) A special graded index anti-reflection (GIAR) porous structure can be integrated with the porous layer to minimize the reflection from the surface. The concept of GIAR coating is very attractive because such structures should provide a broad-band (from UV to NIR) diminishing reflection of 1%-5%



**Fig. 2** – Schematic of s-SWNT/porous a-Si thin film solar cell. SWNTs are grown directly inside nanoporous a-Si layer with GIAR structure. GIAR structure is fabricated by electrochemical etching with gradually changing porosity from high (top) to low (bottom)

for angles up to  $60^{\circ}$ - $80^{\circ}$ , as followed from theoretical models [26]; (vi) Because s-SWNT will be utilized instead of *p*-type a-Si layer it should reduce the total device degradation upon light exposure. This process is called the Staebler-Wronski effect when the defect density of a-Si increases with light exposure, causing an increase in the recombination current and consequently reducing the conversion efficiency.

It is known that similar to crystalline Si, amorphous Si can be electrochemically etched (either to be treated by simple wet etching) to produce straight nanopores or micropores with lengths in the range from submicron to several tens micron. Then the semiconducting enriched SWNTs can be reliably grown inside pores (individual or bundles depending on pore diameter) applying CVD methods. Today, CNT growth by

CVD is a highly controlled process when desired characteristic of CNTs are determined by CVD parameters and can be even optimized with computer simulations and predictive modeling [27].

The current level of stabilized PCE for conventional thin film a-Si solar cells is in the range of 7-9% [28]; therefore, there is a strong demand to increase their efficiency maintaining the same low production cost. The permanent progress in nanostructuring of Si and other group IV, III-V, IV-VI semiconductors in conjunction with novel techniques for CNT growth, sorting, deposition and interface optimization promise further advances in the near future to develop a new generation of hybrid CNT/semiconductor thin, flexible, robust and inexpensive photovoltaics with conversion efficiency exceeding 15%.

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