Exploiting SWCNT Structural Variability Towards the Development of a Photovoltaic Device

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Abstract— **In this paper we propose a conceptual Photovoltaic device that comprises a large number of vertically aligned Single-Walled Carbon Nanotubes (SWCNT) having distinct geometrical structure properties. Through employing analytical models of the CNT, we demonstrate how this structural variation can be exploited in absorbing a broadband of the solar spectra. The results show that given a group of CNTs with a low mean diameter $d_\mu \leq 1$ nm and high diameter spread (d_σ), optimal band-gap variability can be achieved to maximize the potential of absorption within the proposed CNT-based Photovoltaic device.**

Index Terms—**Carbon nanotubes (CNTs), Photovoltaic devices, optical band-gap variation, Monte Carlo simulation, solar spectrum matching.**

I. INTRODUCTION

Single-Walled Carbon Nanotubes (SWCNTs) have been regarded as promising building blocks in a variety of nano-optoelectronic applications due to their distinctive electrical and optical properties [1-4]. Owing to their direct band-gap characteristics, superior carrier mobility, high surface-to-volume ratio and low scattering and recombination losses, nanotubes have been proposed as a potential active material in Photovoltaic (PV) devices [3, 5, 6]. Moreover, a leading property that makes SWCNTs very attractive for PV applications is that depending on their geometrical structure, which consists of the diameter (d) and chirality (θ), they can remarkably exhibit a tunable band-gap [3, 5, 7]. By exploiting this unique trait, more photons of various wavelengths may be absorbed from the solar spectrum compared to a single band-gap material, and hence device conversion efficiencies may be enhanced.

To-date, the growth of SWCNTs with accurate diameter and chirality control using present Chemical-Vapor Deposition (CVD) methods has proven to be a difficult undertaking [8]. Researchers have therefore proposed the adoption of statistical process optimization techniques to optimize the CNT growth process and generate narrowly distributed geometrical characteristics around a desired mean value [8]. Thus, here we computationally examine samples of SWCNTs with various mean diameters (d_μ) and standard deviation (d_σ) that could provide optimal performance for a conceptually proposed CNT-based photovoltaic device. This is carried out by firstly defining analytical models for an isolated SWCNT's optical band-gap energies with respect to its diameter and chirality. We later adopt these models and run Monte Carlo simulations that generate the optical band-gap distributions for typical uncertainties associated with the geometric structure of a vast number of nanotubes. Finally, the band-gap dispersions are compared against the standard solar irradiation spectrum with the aim of identifying the most appropriate CNT structural characteristics for minimal spectral mis-match.

II. SWCNT-BASED PHOTOVOLTAIC DEVICE

The photovoltaic effect of an individual p-n junction carbon nanotube was first studied experimentally in [3] and due to its almost defect free 1D structure an ideal diode behavior was observed [1, 3, 5]. However, the process by which the CNT p-n junction diode was formed involved the intricate use of electrostatic doping from a split gate [3]. Additionally, it was found that defect states in the SWCNT band-gap emerged from the interaction of the CNT with the surface it lay upon, leading to non-ideal behavior [3]. Later, a microcell consisting of a network of SWCNTs was experimentally [6] and theoretically [5] studied where efficiencies were investigated with respect to the electromagnetic coupling and scattering between nanotubes. By nanowelding the SWCNTs across two asymmetric metal electrodes with high and low work functions, respectively, this established a strong built-in electric field along the entire length of the tubes [6]. As a result, efficient separation and collection of electron-hole pairs proceeded once generated by an absorbed photon [6]. Despite the substantial gains in conversion efficiency compared with the first experimental device, still, performance was undermined by the thin mono-layer of widely spaced CNTs used, which scarcely absorbed but a small fraction of the incident power [6]. Also, the introduction of undesirable defect states from interactions with the substrate surface produced high recombination losses. Most importantly, it was found that major improvements to efficiency could ensue with the selection of SWCNTs having band-gaps appropriately matched with the solar spectrum [6].

As shown in Fig. 1, we propose a conceptual PV device comprising a large number of vertically aligned semiconducting SWCNTs with a mean diameter d_μ and diameter variation d_σ contacted between different type Drain and Source metal electrodes. The vertical alignment can be achieved using a standard catalytic-assisted CVD technique or a low-cost postsynthesis deposition method [9].

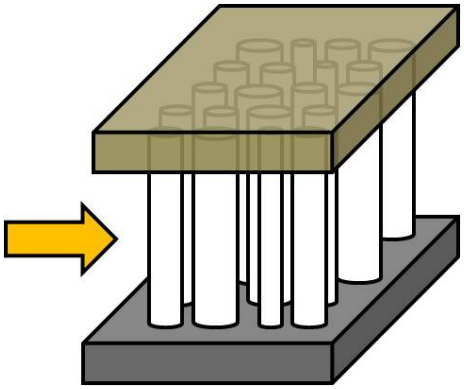

Figure 1. Conceptual PV device with vertically aligned SWCNTs as a photoactive material having diameters represented by d_μ and d_σ. The tubes are contacted between two different type metal electrodes. Electric field of incident light is polarized parallel to nanotube axis.

Recent experimental results indicate that vertically aligned SWCNTs possess robust photoabsorption properties within a very wide spectral range (0.3-2.6μm) [10]. This is because when a photon is not absorbed by a tube it is likely to either be reflected or transmitted towards another nearby tube possibly retaining an alternative band-gap to the first. This 'photon recycling' process may proceed from one layer of tubes to another until the photon ultimately interacts with a CNT having a corresponding band-gap energy or lower. As an outcome, the reflectance of a sample of vertically aligned SWCNTs was measured to be 0.01-0.02 only across the entire spectral range [10]. However, it was reported that the photoresponsitivity and carrier collection can be significantly reduced with the entanglement of tubes [5]. Therefore, it would be necessary to ensure sufficient separation and adequate alignment amongst SWCNTs when used for our proposed PV device. It has also been experimentally and theoretically confirmed that nanotube photoabsorption could be maximized when the electric field of the incident light is polarized parallel to the tube axis as indicated in Fig. 1 [5, 10].

A potential improvement to the device depicted in Fig. 1 can include the combination of CNT samples with descending d_μ facing the incoming light first so as to have higher band-gap tubes absorbing the shorter wavelength photons.

Due to the complexity associated with accurately measuring and probing such a proposed device, computational simulations may be performed to gain valuable insight on the tube geometries required for optimal operation.

III. Analytical Model for Isolated SWCNT Optical Band-Gap Energies

When a semiconducting SWCNT is optically excited, a band-to-band transition (i.e. the resonant excitation of an electron from the valence band to the conduction band) occurs, which in turn generates photocurrent and a photovoltage [1, 11]. In the following section we produce analytical models that describe the SWCNT transition energies (E_{ii}) as a function of the tube geometry.

Several theoretical and analytical models have been established to simulate the electronic band structure and optical properties of SWCNTs [8, 11]. The most commonly used is the nearest-neighbor Tight-Binding (TB) approximation with zone-folding, which has been experimentally verified, however, it can be computationally intensive and would be very difficult to utilize in a timely manner if millions of distinct CNTs need to be analysed simultaneously [8, 11]. In addition, it was revealed in [12] that the third-nearest neighbor TB approach yielded better fitting results for the transition energies when compared to first-principle *ab initio* calculations [13].

Thus, a simulation was run using the third-nearest-neighbor TB approach in conjunction with the zone-folding technique to calculate the transition energies for a set of 286 SWCNTs. These tubes were characterized by all possible chiralities, θ=0^0-30^0, and diameters (d) ranging between 0.5nm-2.55nm. Fig. 2 shows the calculated transition energies for various θ and d.

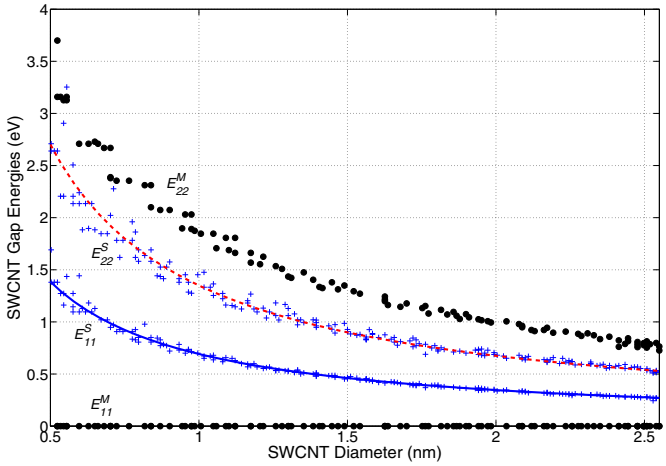

Figure 2. SWCNT transition energies vs. tube diameter for chiralities in the range 0^0-30^0. + (●) represent semiconducting (metallic) tubes. — (---) corresponds to Eq. 1 (Eq.2) obtained using regression analysis.

From Fig. 2 it could be seen that the data points are very much similar to the optical transition curves outlined by the Kataura plot in [14], although our values have an additional accuracy for the smaller tube diameters and certain chiralities as more distant neighbors are considered in the TB model employed [13, 15].

Since we are concerned with the semiconducting tubes only, the first and second excitation transition energies (prescribed as E_{11}^S and E_{22}^S) are of interest. Using a curve-fitting and regression technique we were able to model the corresponding data points in Fig. 2 and generate the following relationships:

$$E_{11}^S = \frac{0.692}{d} \quad (1)$$

$$E_{22}^S = \frac{1.356}{d} \quad (2)$$

Equations (1) and (2) predict the semiconducting transition energies with a Normalized Root-Mean-Square (NRMS) error

of 1.75% and 3.8%, respectively, when compared to the third-nearest-neigbor TB with zone-folding results. These relations confirm that the band-gaps are proportional to $1/d$ and the constant of proportionality is independent of θ, which has been further verified in [8, 16]. More interestingly, the E_{22}^S / E_{11}^S ratio yields 1.96, which is slightly lower than that measured experimentally (2.00) in [17].

IV. Comparing SWCNT Optical Band-Gap Distribution with Solar Irradiation Spectra

In the following section we initially define the probability functions chosen to replicate a realistic spread in SWCNT diameter and chirality. By taking advantage of the optical transition energy models derived in the previous section and varying the distribution properties we simulate the corresponding band-gap dispersions, which are subsequently compared with the AM1.5 solar energy spectrum and statistically analyzed.

A. SWCNT diameter distribution

Recently, in [18] it was proposed that at any given CVD process condition, so long as the carbon feeding rate is fixed there is an optimal diameter of nanoparticles that nucleate nanotubes [8]. Thus, assuming that the process of defining the catalyst particle size can be optimized to give a narrow distribution around a specified d_μ, we can expect that as the number of fabricated SWCNTs increases significantly for a given batch, the spread in diameter will converge towards a Gaussian spread [8].

B. SWCNT chiral angle distribution

Unlike the SWCNT diameter, controlling the chiral angle can be more intricate resulting in a commonly observed homogeneous spread within a collection of synthesized nanotubes [8]. Hence, for our study, it is reasonable to assume a uniform random distribution in the CNT chiral angle.

C. Semiconducting SWCNT optical band-gap distribution

Here, the variation in CNT optical band-gap is determined by firstly executing an analytical expression derived in [8] to distinguish whether a tube is metallic or semiconducting over a large number of samples ($1.5\text{x}10^5$) that are randomly generated from the selected structural distributions outlined above. If the tube is found to be semiconducting then the optical transition energies of Eq. (1) and (2) are evaluated.

For each run of our Monte Carlo simulation the diameter distribution properties d_μ and d_σ were varied between the ranges 1.01-1.71nm and 0.04-0.2nm, respectively [8]. Fig. 3 depicts a density estimation of a subset (d_μ=1.01nm and d_σ=0.04-0.2nm) of semiconducting CNT optical band-gap results.

D. Distribution comparison using a statistical test

Fig. 4 represents a histogram comparing the optical band-gap distribution generated for a Gaussian spread in diameter (d_μ=1.01nm and d_σ=0.2nm) with the standard AM1.5 Solar Irradiance Spectrum given in [19]. Qualitatively, it could be observed that the CNTs optical band-gap energies are well matched with the IR and lower visible regions (~0.6-2.6μm) of the solar energy spectra.

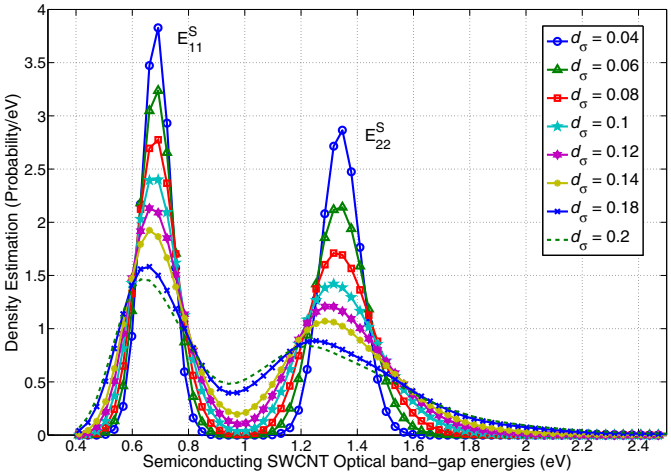

Figure 3. Density estimation of semiconducting SWCNT optical band-gap energies obtained from Monte Carlo simulations for a Gaussian spread in diameter with d_μ=1.01nm and d_σ=0.04-0.2nm.

In quantifying the optimal SWCNT structural properties for our proposed PV device we performed a two-sample Kolmogorov-Smirnov test to compare each optical band-gap distribution with the AM1.5 Solar Irradiance Spectra. This generated a value representing the difference as a percentage.

Fig. 5 illustrates a set of curves that generally show an increasing mis-match between the solar spectra and the CNT optical band-gap distributions with higher mean diameters (d_μ). Further, as expected, the spectral mis-match is intensified with lower variations in CNT diameter (d_σ). Accordingly, we propose that the ultimate SWCNT geometric properties for the PV device of Fig. 1 should comprise a mean diameter ≤ 1nm and a high diameter variation.

The lowest mis-match recorded is just under 50% for d_μ=1nm which is in good agreement with recommendations made in [3] where it was claimed that SWCNTs having diameters around 0.8 nm would offer significant improvements in PV conversion efficiency.

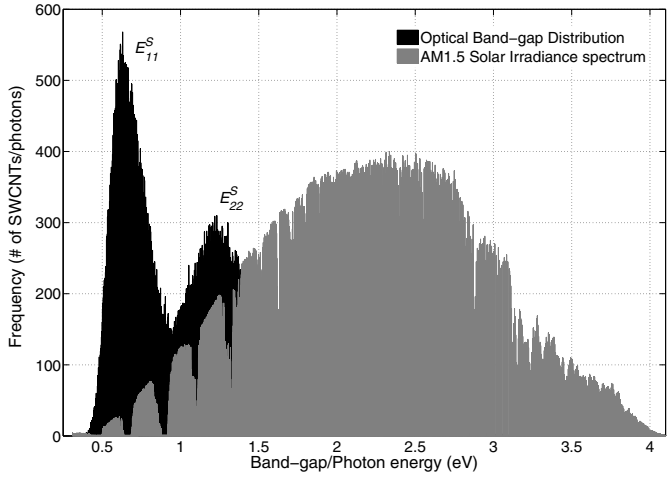

Figure 4. Histogram comparing semiconducting SWCNT optical band-gap distribution (for d_μ=1.01nm and d_σ=0.2nm) with AM1.5 solar energy spectra.

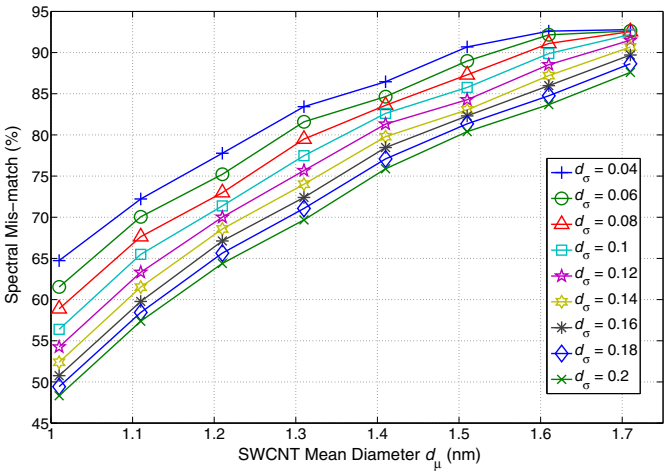

Figure 5. Graph representing the mis-match as a percentage between the solar spectra and CNT optical band-gap distributions. Mis-match is given with respect to different d_μ and d_σ.

V. CONCLUSION

In this paper we propose a conceptual photovoltaic device consisting of vertically aligned semiconducting SWCNTs with a range of band-gap energies corresponding to the geometrical structure variation. Using a Monte Carlo approach we show that the band-gap variability can potentially be exploited to absorb a broadband of the solar energy spectrum, particularly in the IR region. Most notably, simulated results reveal that a set of SWCNTs with a mean diameter $d_\mu \leq 1$ nm and high diameter dispersion (d_σ) provide the optimal spectral match.

In our future work we shall address the effect of structural variation on the PV conversion efficiency as well as the possible methods that could be utilized in realizing the proposed device.

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