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2009 Nanotechnology 20 035203

(http://iopscience.iop.org/0957-4484/20/3/035203)

Nanotechnology **20** (2009) 035203 (7pp) doi:10.1088/0957-4484/20/3/035203

Alignment enhanced photoconductivity in single wall carbon nanotube films

Ye Liu[1], Shaoxin Lu[1] and Balaji Panchapakesan[1,2]

[1] Delaware MEMS and Nanotechnology Laboratory, University of Delaware, Newark, DE 19716, USA
[2] Department of Mechanical Engineering, University of Louisville, KY, USA

E-mail: b0panc01@louisville.edu

Received 28 July 2008, in final form 21 October 2008
Published 16 December 2008
Online at stacks.iop.org/Nano/20/035203

Abstract

In this paper we report, for the first time, the alignment enhanced photoconductivity of single wall carbon nanotube films upon laser illumination. The photoconductivity exhibited an increase, decrease or even 'negative' values when the laser spot was on different positions between contact electrodes, showing a 'position' dependent photoconductivity of partially aligned films of carbon nanotubes. Photon induced charge carrier generation in single wall carbon nanotubes and subsequent charge separation across the metal–carbon nanotube contacts is believed to cause the photoconductivity changes. A net photovoltage of ∼4 mV and a photocurrent of ∼10 μA were produced under the laser intensity of ∼273 mW with a quantum efficiency of ∼7.8% in vacuum. The photocurrent was observed to be in the direction of nanotube alignment. Finally, there was a strong dependence of the polarization of the incident light on the photocurrent and the orientation of the films influenced the dynamics of the rise and fall of the photocurrent. All of these phenomena clearly have significance in the area of design and fabrication of solar cells, micro-opto-mechanical systems and photodetectors based on carbon nanotubes.

1. Introduction

Single wall carbon nanotubes (SWNTs) are unique nanomaterials with remarkable optical properties. In recent years, many studies have been performed on the optical properties of SWNTs to fulfill their promising applications in optics and optoelectronics. Specifically, nonlinear optical properties [1, 2], optical limiting behavior [3], Raman scattering [4], photoluminescence [5], electroluminescence [6], photon induced molecular desorption [7], and radioactive properties [8] of SWNTs have been intensively studied. Many prototype devices and possible applications, such as ultra fast optical switching [9], nanotube antennas [10], large area transparent electrodes [11], photodetectors [12] and solar cells [12] have been proposed. While much of these reports have placed emphasis on nanosize devices, there has been a growing trend for SWNTs merging into micro- and macroscopic devices to provide more practical applications, as the synthesis cost of SWNTs are expected to decrease [13]. Nanotubes are not only used as optoelectronic material, they also have excellent mechanical properties. Studies on carbon nanotube films may provide us opportunities for constructing smart structures with multiple functionalities. For example, in the fields of flat and flexible display, photodetection and flexible solar cells capable of covering non-flat surfaces, the application of macro scale multi-functional carbon nanotube ensembles is essential. Recently, nanotube thin film based micro-opto-mechanical systems has been reported whose working principle is based on the photo-mechanical actuation of carbon nanotubes [14–18]. A number of micro-opto-mechanical systems were demonstrated including nanotube based micro-mechanical actuators [15, 16], nanotube based micro-grippers [17, 18] and nanotube based micro-mirrors [19]. The driving mechanisms of photo-mechanical actuation include electrostatic, elastic, optical, and polaronic interactions in carbon nanotube networks and thin films. Studying the dependence of alignment of carbon nanotubes in thin films/fibers on photoconductivity can benefit the design and fabrication this new and upcoming area of micro-opto-mechanical systems based on carbon nanotubes. Recently double walled nanotube based solar cells whose power conversion efficiency of 1% was reported [20]. These devices reported network of carbon nanotubes that were non-oriented

between contact electrodes. The design, fabrication and performance of these devices could be improved by gaining knowledge on how alignment of nanotubes in thin films along their axis enhances their photoconductive properties.

Photoconductivity of carbon nanotubes has been studied both in the past in nano, micro and macroscopic samples. In past studies, single carbon nanotube with two contact electrodes, in the form of a nanotube transistor, was employed to study the photoconductivity of single nanotube or small bundles [21–24]. An estimated quantum efficiency of 10% was reported in these studies for single nanotubes [24]. A photocurrent due to photon induced electron–hole pair generation and subsequent charge separation by an electrical field was found flowing through the sample upon light illumination. In these nanodevices, the possible effect of metal electrodes on the photoconductivity either through the molecular photodesorption of metals [21] or through the modulation of the Schottky barrier height [24] was reported. Photoconductivity in micron and macroscopic samples of carbon nanotubes revealed a position dependent photoconductivity showing the effect of the position of the electrodes on the photoconductivity of thin films. In these studies the effect of pressure and light pulse frequency was studied. An experimental quantum efficiency of 1.5% in vacuum was reported for these non-oriented films of carbon nanotubes [25].

In this paper, we show the enhancement of the photoconductivity due to partial alignment of nanotube in films. Partially oriented and non-oriented samples of single wall carbon nanotube films were studied for the photoresponse both in air and vacuum. These films consisted of thousands of interconnected nanotubes joined by van der Waals forces. The experiments revealed strong photoresponse for both oriented and non-oriented samples showing strong charge separation at the metal–nanotube interface. One of the most intriguing aspects of these experiments was the dependence of power conversion/internal quantum efficiency on the orientation of the nanotube in the samples. Further, the polarization of the incoming light had a dramatic effect on the photoresponse of the oriented nanotube samples depending on whether the samples were parallel or perpendicular to the direction of electric field of the incoming light. All these effects could be of practical use in the design and fabrication of photodetectors and solar cells based on carbon nanotubes.

2. Experimental details

Pure nanotube samples being studied include: unaligned SWCNT and partially aligned SWCNT fibers. Unaligned nanotube ensembles were prepared in the form of nanotube films by vacuum filtration of nanotube suspensions. Commercially obtained SWNTs were dispersed in isopropyl alcohol and agitated for 20 h to make a uniform nanotube suspension with a concentration of $\sim$0.1 mg ml^{-1}. The SWNT suspension was then flown through a poly(tetra-fluoro-ethylene) filter in a vacuum filtration set up. The resulting SWNT sheet on the filter was rinsed with isopropyl alcohol dried and was then peeled off the filter with a final thickness of $\sim$15 μm and a bulk density of $\sim$0.3 g cm^{-3}. The nanotube sheets produced in this way had a sheet resistivity of $\sim$0.5–5 $\Omega/\square$. The nanotube sheet was then cut into long strips of $\sim$2 mm $\times$ 20 mm in size. Platinum electrodes were fabricated using conventional lithography, metal deposition and lift off processes on glass slides because of its transparency for easier experimental set up. Experiments done on silicon dioxide wafer also gave very similar results. These procedures have been reported in the past to study the position dependent photoconductivity of carbon nanotube thin films [25].

To produce partially aligned SWCNT fibers, SWCNT suspensions were diluted to $\sim$5 μg ml^{-1} to better separate the nanotube bundles by long ultrasonic agitation. A vacuum filtration setup was modified to accommodate an airbrushing head for injecting CNT suspensions to the funnel. A mixed cellulose ester (MCE) filter was used for the ease of filter removal in post processing. When the CNT suspensions were introduced to the filter surface by airbrushing in a fixed direction, nanotubes aligned themselves in this flow direction, while the solution was pumped off from the filter by the vacuum, leaving a mass amount of partially aligned SWCNTs on the filter surface. After $\sim$300 nm of CNT films were deposited on the filter, the nanotube bearing MCE filter was removed from the system, dried, and cut into long strips along the flow direction, which was followed by filter dissolving in multi-baths of acetone and isopropyl alcohol. Then the resulting CNT strips floating in the solution were dragged out of the solution while rotating in a fixed direction. The strong surface tension of the solution served to collapse the CNT strips to form partially aligned CNT fibers. This well established procedure produces single wall nanotube fibers about 0.8–10 μm in diameter and 1–10 mm in length, with nanotubes and bundles favorably aligned in the direction of the fiber axis. This procedure has also been reported in the past for studying the alignment dependent mechanical responses of nanotube films to light [14, 26]. An 808 nm semiconductor laser, which was collimated to a rectangular light spot of $\sim$1 mm$\times$2 mm,was used as the light source. The light intensity was recorded using a Newport 1815-C intensity meter. An Agilent 4156C semiconductor parameter analyzer was used for the current and voltage measurements, because of its short response time (smaller than 1 ms) and accuracy in current measurement (better than 1 fA).

3. Result and discussion

3.1. 'Position' effect of photoconductivity in non-oriented and oriented carbon nanotube thin films

Figure 1 is the SEM image of the aligned carbon nanotube thin films rolled in the form of a fiber. For comparison, the insets show the SEM images from both non-oriented and oriented carbon nanotube thin films. The upper inset in figure 1 shows the nanotubes oriented partially along the fiber axis and the lower inset shows the non-oriented film. While there are no methods reported to produce perfectly aligned single wall nanotube fibers or films to date, current ways of making aligned single wall nanotube fibers rely on flow assisted

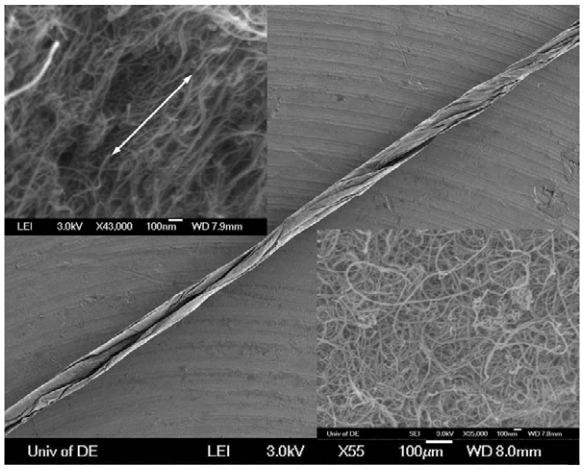

Figure 1. SEM image of a partially rolled thin film of carbon nanotubes; inset compares the non-oriented (bottom) and partially oriented (top) samples.

alignment approaches [26]. As shown in the upper inset of figure 1, most of the nanotubes are partially aligned to the fiber axis or oriented themselves within a small angular range of 40° with respect to the fiber axis. Such partial alignment would significantly affect the optical and electrical properties of the nanotube ensembles. We have shown in a previous study that such partial alignment as shown in the lower inset of figure 1 affect the collective mechanical properties of nanotube ensembles to light [14].

Figure 2(a) schematically showed the sample with the nanotube sheet of ∼2 mm × 20 mm on top of the platinum electrodes, which were 1 mm in width and 10 mm apart from each other. From the top view of the sample in figure 2, an alphabetic sequence from A to E showed the five different testing positions where laser spot would illuminate. The shaded area in the figure indicated that the laser spot of ∼0.7 mm × 2 mm was on position C, which was the center of the sample. Positions B and D were positive and negative electrodes, respectively, while position A and E were 1 mm away from the outer edge of the electrodes. Laser pulses of 0.1 Hz with 50% duty cycle and 80 mW intensity was illuminated normally to the sample surface. A small voltage of 100 μV was applied to the sample during the measurement to ensure that the background current was small enough to eliminate the effect of joule heating [27]. Rather than similar responses that would normally be expected, the photocurrent of the sample exhibited different responses when the light spot was on different positions as shown in figure 3. When the laser spot was directed on the nanotubes on top of positive electrodes (position B), an increase in photocurrent from a dark value of −1.1 to ∼3.6 nA was observed. However, when the laser spot was directed at the nanotubes on top of the negative electrodes (position D), there was a dramatic decrease in photocurrent from the dark value to ∼−7.2 nA, which indicated that this current flowed in the 'reverse' direction, although the voltage was still forward biased. This 'position effect' was first reported in our previous research on non-oriented carbon nanotube films [25]. Similarly in the partially

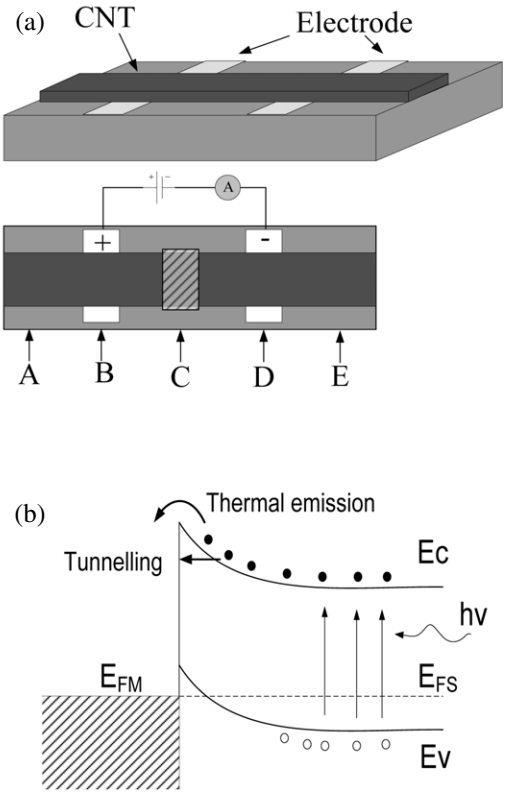

Figure 2. (a) Schematic drawing of the carbon nanotube sheets under testing. The bottom part shows the top view of the device. A–E were five testing positions on the sample where a laser spot was pointed. The shaded area indicates that the laser spot was on position C. (b) Band diagram of carbon nanotube (right) in contact with platinum electrodes (left).

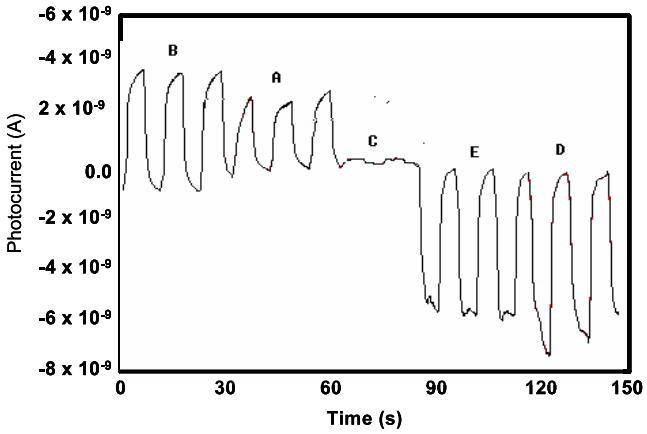

Figure 3. The photocurrent of carbon nanotube sheets when the laser spot was on different positions (from A to E) of the sample.

aligned fibers, photocurrent like this showed that the positive electrode had the effect of increasing the forward current, whereas the negative electrode had the effect of increasing the backward current. A possible reason for this phenomenon is that a built-in potential exists between the electrode and the nanotubes under light illumination, which would separate the as-generated electron–hole pairs, and push the electron

into the electrodes, while leaving the holes in the carbon nanotubes. Similarly to the unaligned films, when laser light was illuminated on position A and E, which were beyond the range of two metal electrodes (not in the circuit), the changes of photocurrent similar to that of position B and D respectively, were still observed, although the amplitude of the changes were smaller. When the laser spot was in position C, a much smaller photocurrent change was witnessed. Repeating all the above experiments with a halogen lamp of 120 mW cm^{-2} intensity as the white light source resulted in similar responses. However, if the whole nanotube sample was illuminated by light, then the change of photocurrent (increase) was quite small with only a few percent of dark current. These results indicate that there were light induced build-in potentials at both electrodes which were opposite and competing with each other in determining the sample current. The differences in the position dependent photoconductivity between non-oriented and oriented samples were mainly in the amplitude of the current. For non-oriented samples, there was a steep increase in the photocurrent compared to the partially oriented fibers. However, both the non-oriented and oriented samples followed the same pattern of photoresponse. The amplitude of the photocurrent in the oriented samples were quite small due to the smaller number of nanotubes in the sample. The fiber in our experiment bears a radius as $\sim$1 μm, thus its cross-section area is $\sim$3.14 μm^2; so that its max current density would be $\sim$0.2 A cm^{-2} with an incident light intensity of 137 mW. Similar calculation can bring out the maximum current density of non-oriented film samples in [25] has a current density of $\sim$0.3 A cm^{-2} with the same light intensity; comparing this result to the previous calculated value of the aligned fiber, we can see that the current densities is of the same order, which indicates the small current of aligned fibers is caused by the fewer number of nanotubes in the oriented fiber.

Similar to our previous study on non-oriented nanotube films, our experiments on partially oriented nanotube fibers further demonstrated that the molecule photodesorption effect becomes less pronounced when the wavelength of incident light is at 808 nm, approaching the near IR region [25]. So to explain the original cause of photocurrent, metal–carbon nanotube contacts have been studied previously and an energy band diagram similar to that of figure 2(b) is suggested, which stands for the band diagram in ideal contact conditions [25, 28, 29]. When the carbon nanotubes were illuminated, photon energy was absorbed by the nanotubes, resulting in generation of electron–hole pairs or excitons [10]. These carriers would diffuse in carbon nanotubes randomly when there was no or only small electrical field in the sample. As they approach the metal–nanotube interface, the hot electrons might have enough energy to go across the Schottky barrier via tunneling or thermal emission and enter the metal before they recombine with holes, as shown in figure 2(b).

3.2. Dynamic response of photoconductivity of partially oriented single wall carbon nanotube thin films

Partially oriented samples of carbon nanotubes were studied for their dynamic response. By varying the laser intensity on the negative electrode of the sample, the amplitude of the photocurrent as a function of laser intensity was recorded in figure 4, which shows a linear dependence between these two parameters. The dynamic response of the photocurrent was measured when laser pulses of 25 mHz with a 50% duty cycle were used to excite the sample. Figure 5 shows in line L_1 the corresponding photocurrent increase of oriented CNT fibers, comparing to the photocurrent increase of a similar dimension of non-oriented film in Line L_2, respectively. In both curves, the experimental data fit well into the exponential form of: $I = I_0 + A_1 \exp(-\frac{t}{t_1})$, respectively. The first order exponential fit for Line L_1 gives out a time constant t_1 of $\sim$0.9, while the fit for line L_2 gives out a t_1 of $\sim$2.1. This shows that the oriented nanotube samples showed faster response than non-oriented samples.

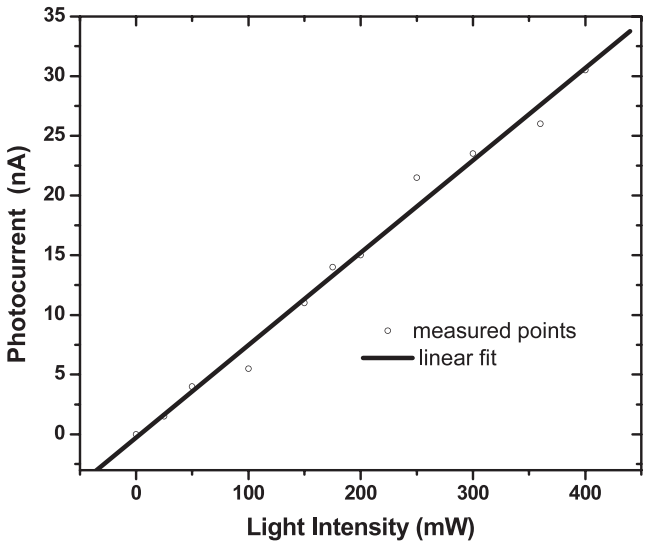

Figure 4. The amplitudes of photocurrent as a function of laser intensity. Measurements were done in room atmosphere.

When the same aligned CNT sample was illuminated by light pulse with a varying frequency from 50 mHz, 250 mHz, 1 Hz, 5 Hz to 20 Hz, while the laser intensity was kept at 137 mW, the sample exhibited a rapid decrease in photocurrent amplitude with respect to the increase in pulse frequency, as shown in figure 6. This was also seen in the past for non-oriented CNT films.

3.3. V–I characteristics

As the photocurrent response involves optical to electrical energy conversion mechanism, a possible application of this technology may be solar cells, photodetectors and energy scavenging devices. Using several oriented samples, we measured the V–I characteristics of the sample under a constant light intensity of $\sim$247 mW directed at the negative electrode in vacuum as well in room atmosphere. Figure 7 shows the V–I curves of the sample, with and without laser illumination. The curves are obtained by applying a sweeping voltage from -4 to 4 mV. A P–N junction rectifying behavior was witnessed from both of the curves when the voltage range is within $\pm$2 mV, indicating the existence of

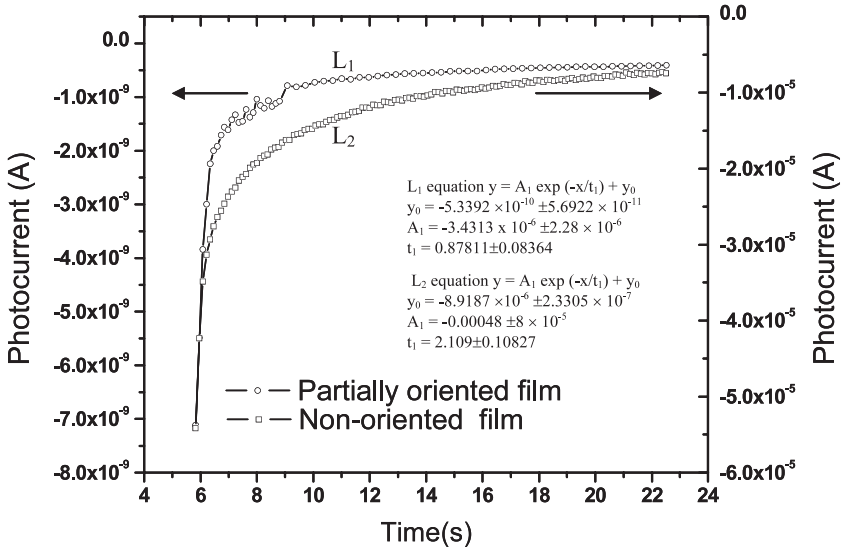

Figure 5. Dynamic responses of photoconductivity and the parameters of their exponential fit. The measurement was done in standard atmosphere pressure, with a light pulse of 25 mHz frequency and 137 mW of laser intensity.

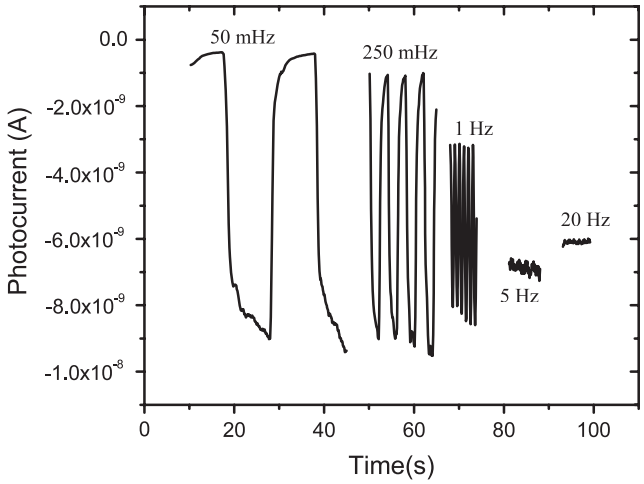

Figure 6. The photocurrent of a nanotube fiber when laser pulses of different frequencies were illuminating the sample. Photocurrent as a function of laser pulse frequencies.

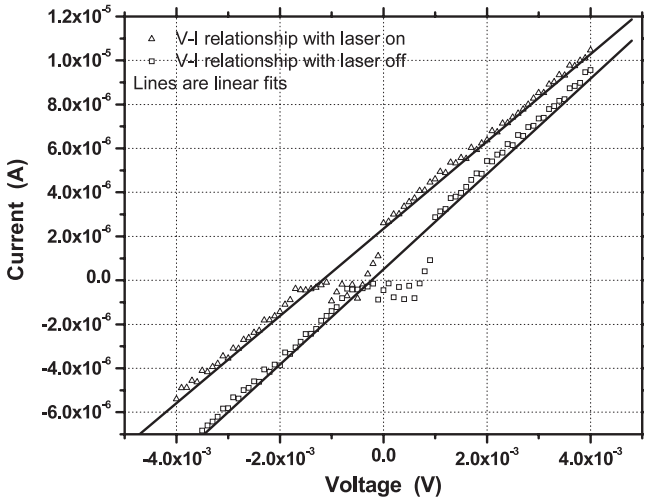

Figure 7. V–I characteristics with 247 mW laser illumination.

a Schottky barrier at the electrode–fiber contacts. However, a linear dependence was shown when the applied voltage went beyond 2 mV. The single wall nanotubes in this study were produced by laser ablation process and the samples contains both semiconducting and metallic nanotubes. The electrical behavior of the mixture of semiconducting and metallic tubes depends on the sample construction and its contacts with electrodes. While macroscopic samples of nanotube ensembles generally produce ohmic characteristics, smaller samples produce electrical characteristics similar to that of individual tubes. The micro sample size in this study is between the extremes of the above cases, thus exhibiting a blend of rectifying and ohmic behavior. Under small electrical field, sample exhibit rectifying behavior and current was limited by the contact between the electrode and nanotubes and inter-nanotube contacts. Under higher voltage, the V–I dependence becomes linear as a result of the increased current path through the nanotube networks, which is due to increased electrical field to overcome the potential barriers for charge transportation. Further, it is shown in figure 7 that under illumination on the electrode position, the sample showed an open-circuit voltage of ∼0.15 mV and close-loop current of ∼2.5 μA. While these values are strongly dependent on light illumination, they are also interrelated by the contact resistance and sample bulk resistance. Optimization of sample construction such as using perfectly aligned nanotube bundles, increasing electrode contacting area, improving nanotube purity will play significant role in leveraging the two values toward practical applications.

A constant photocurrent of ∼2.2 μA is obtained from the difference in both the curves with an experimental quantum efficiency of ∼2.5% in room atmosphere for the partially oriented samples. Past theoretical work had predicted that

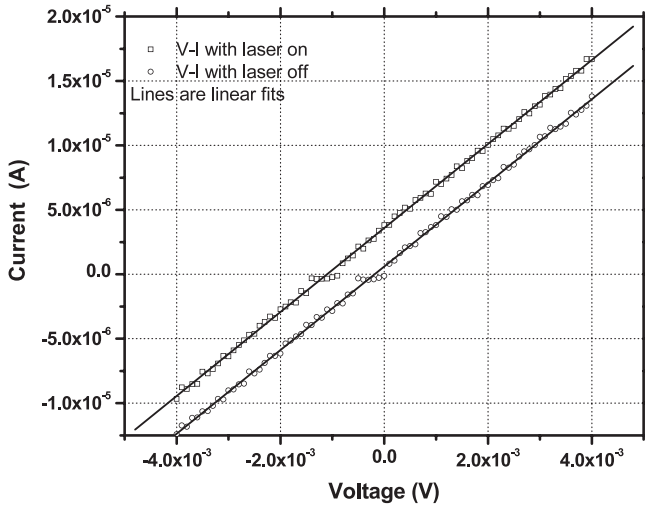

Figure 8. V–I characteristics with laser on and off in 300 mTorr.

a single nanotube have a quantum efficiency of larger than 10% [24]. Experimental work on non-oriented nanotube thin films showed a quantum efficiency of ∼1.5% in vacuum. Our results are the first to show that by partially orienting the nanotubes in samples, one can improve the dynamics and the power conversion efficiency. Figure 8 shows the V–I characteristics in at 300 mTorr. A photovoltage of ∼4 mV and current of ∼5 μA resulted thereby achieving an internal quantum efficiency of ∼7.8%. These are the first experimental evidence to show that such large internal quantum efficiency is quite possible in nanotube thin films. Our results show that there is considerable room for improvement. As the separation of semiconducting nanotubes from metallic ones has become more practical in recent years [30, 31] one can use better nanotube samples with more proportion of semiconducting nanotubes to increase the device efficiency. In current samples, metallic carbon nanotubes have large energy band gaps due to M11 transitions between van Hove singularities and they are much larger than that of semiconducting nanotubes which correspond to S11 or S22 transitions between van Hove singularities [32, 33]. So metallic nanotubes can only absorb near infrared light to cause intraband transitions instead of interband transitions required for electron–hole pair generation. Further, the films used in this study were partially oriented nanotube thin films. By having much high degree of orientation one can even achieve more than ∼10% power conversion efficiency. By having arrays of such devices, one could achieve large power conversion efficiencies in nanotube based solar cells. Comparing the samples with non-oriented samples, partial orientation of nanotubes in samples produced faster response, position dependent photoconductivity and achieved much higher internal photon to electron power conversion efficiency. These could be used as design parameters for future nanotube based solar cells.

4. Conclusions

In this paper we have shown the differences in photoconductivity between non-oriented and partially oriented thin films of carbon nanotubes. Partially oriented thin films of nanotubes were produced by combination of vacuum filtration and flow induced alignment technique. These samples were then studied for photoconductivity. Partially oriented nanotube thin films exhibited similar position dependent photoconductivity as non-oriented samples. However the amplitude of photocurrent was small owing to the fewer number of nanotubes in the oriented samples. Studies on dynamic response showed that the partially oriented nanotube samples produced faster response compared to non-oriented samples. Partially oriented samples also showed ∼2.5% power conversion efficiency in room atmosphere and 7.8% efficiency in 300 mTorr. While there is considerable room for improvement, these results show that nanotube thin films could be quite applicable for solar cells, micro-opto-mechanical systems and photodetectors.

Acknowledgment

Funding for this research was partially supported by NSF CAREER award ECS 0546328 for BP.

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