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Large photocurrent generated by a camera flash in single-walled carbon nanotubes

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Abstract
The photocurrent generated in single-walled carbon nanotube bundles upon camera flash illumination has been studied under different ambient pressures and light intensities. The results show that the intensity of photocurrent depends closely on the ambient pressure and light intensity. With the ambient pressure reduced, the photocurrent exhibits a logarithmic growth behaviour. Meanwhile, the photocurrent increases with the increase in light intensity. In this work, a dynamic model is employed to unveil the origins of the observed photocurrent. A much smaller lifetime of photocarriers ($\sim$10 ms) is observed than that needed for gas molecular desorption or photodesorption (seconds or longer). Our results are consistent with the model of Schottky barriers being responsible for photocurrent generation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Single-walled carbon nanotubes (SWNTs) have been regarded as promising building blocks for nanoelectronics because of their one-dimensional character and unique electronic structure [1]. Recently, the photoconductivity of carbon nanotubes has attracted intensified interest due to their potential use in optoelectronic devices [2–5]. The samples have covered both micro- and macro-devices. Zhang and Iijima [6] first observed the photocurrent in the SWNT filaments and attributed it to phonon-induced electron–hole pair generation and subsequent charge separation upon laser irradiation. Fujiwara [7] and Levitsky [8] examined the photocurrent in thin nanotube films and attributed it to gas molecular desorption from carbon nanotubes. Oxygen absorption [9, 10] indeed has a doping effect on carbon nanotubes, which changes the nanotubes from an intrinsic n- to p-type semiconductor. However, there is still disagreement on whether it occurs at electrodes or nanotubes and how it affects the observed phenomenon. Subsequent works on carbon nanotube field-effect transistors (CNT-FETs) [11–17], SWNT sheets [18] and films [19] imply that the Schottky barrier existing at the metal-nanotube contacts should be responsible for the observed photocurrent. More recently, experimental works suggest that the major photoexcitations are excitons, rather than free carriers [20–23]. The exciton model is supported by recent experiments on the relaxation of photoexcitations [23], two-photon excitation spectroscopy [24] and optical spectra [25] in SWNTs. However, the mechanisms of charge separations from the excitons are not clear. Therefore, it is significant to clarify the origin of the photocurrent. In addition, previous works mainly focuses on the photoresponse of carbon nanotubes to laser, infrared and ultra-violet (UV). Thus it is necessary to investigate the photoresponse of carbon nanotubes to a camera flash. In this paper, we report the large photoresponse of macro-scale SWNT bundles under a camera flash. We find

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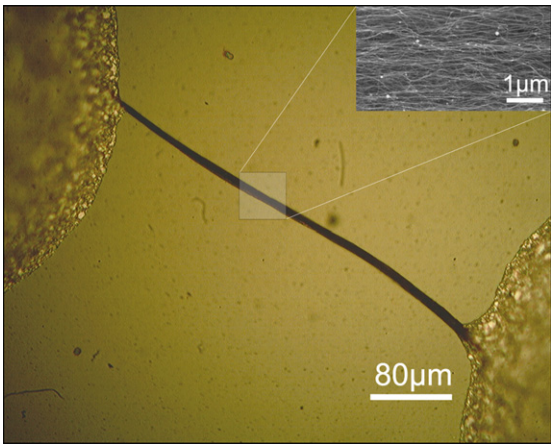

Figure 1. Optical image of the two-terminal device. The inset is the typical SEM image of SWNT bundles.

that a large photocurrent can be generated in macro scale SWNT bundles using a camera flash as a light source. The photocurrent can be deeply affected by the ambient pressure and light intensity. Compared with the typical lifetime of photocarriers (∼10 s) of the gas molecular desorption mechanism, we get a much smaller one (∼10 ms) based on a dynamic model. Our results are consistent with the model of Schottky barriers being responsible for the observed photocurrent.

2. Experimental

SWNTs used in this work were synthesized by floating catalytic chemical vapour deposition (CVD) [26, 27]. Figure 1 (inset) shows the typical scanning electron microscopy (SEM) image of aligned SWNT bundles. An as-prepared SWNT bundle was first transferred onto a silicon wafer with a 200 nm SiO_2 layer. Two silver paint drops were placed on it, which were connected to two platinum wires. Figure 1 shows the optical image of the device prepared in this way, where the bundle has a diameter of ∼3 μm and a length of ∼1.3 mm. During the photocurrent measurements, a small voltage (−25 μV) was applied to the sample to exclude the effect of Joule heating [8]. The resistance is ∼2.2 kΩ at room temperature in air. A commercial camera flash with three different light intensities (M/16, M/4 and M, M = 100 mW cm^{-2}) was used as the illumination source, which has a typical flash time of ∼1 ms. The filling gas and the window material used in the camera flash are xenon (Xe) and synthetic silica, respectively. The light produced by the camera flash was introduced into SWNT bundles through a quartz glass window on the sample chamber. A Keithley 4200 semiconductor characterization system was employed to monitor the current variation under illumination. It has a short response time (smaller than 8 ms) and high accuracy in the current measurement (better than 1 pA). A vacuum system was employed to study the effect of the ambient pressure on the photocurrent. The experiments were carried out from 10^5 to 10^{-3} Pa vacuum.

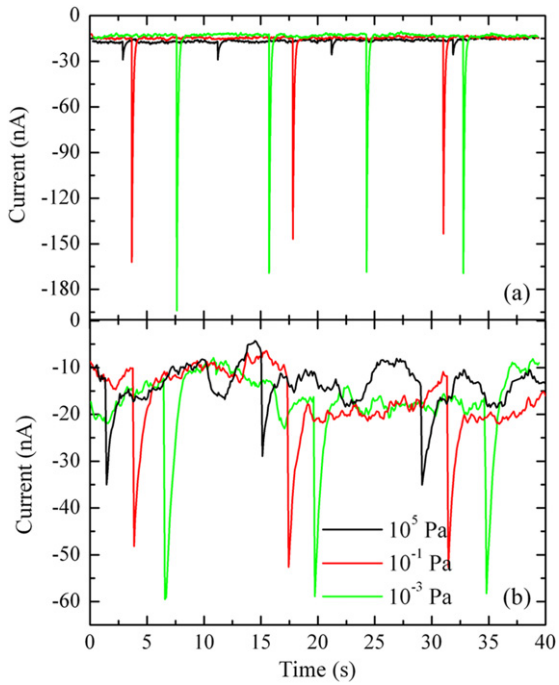

Figure 2. The dynamic characteristics of current with time and the effect of ambient pressure on the photocurrent of SWNT bundles measured at room temperature. (*a*) and (*b*) are the experimental results of initial cases in air and oxygen gases.

3. Results and discussion

Figure 2(*a*) shows the photoresponse of SWNTs to M/16-level illumination with air as the initial gas. It can be seen that there are two major characteristics in the current curves. One is the prompt response of SWNTs to light illumination and the other is that the photocurrent exhibits a rapid increase behaviour with the ambient pressure reduced. If I and I_0 represent the photocurrent and dark current, we find that the current increased from the dark current of ∼ −14 to −30 nA, −162 nA and −194 nA as the ambient pressure (P) reduced from 10^5 to 10^{-1} Pa and 10^{-3} Pa, respectively. To quantitatively investigate the ambient pressure dependence of the photocurrent, we obtained the photocurrent $I(P)$ at each ambient pressure P averaged from the photocurrents at different illuminating times. Figure 3 plots the ratio of the photocurrent to the dark current (I/I_0) in a semi-logarithmic scale. By fitting the experimental data, a logarithmic dependence of the photocurrent on the ambient pressure, $I = I_0(9.87 - 0.73 \ln P)$, was observed. This monotone behaviour of the photocurrent's dependence on ambient pressure is qualitatively consistent with the previous works [18, 28]. However, the physical origin was not clear at present. To answer this question, we further investigated the photocurrent in different gas atmospheres, such as argon, oxygen and nitrogen. As an example, figure 2(*b*) only shows the experimental results in oxygen. With the same method as that which treated the data in figure 2(*a*), I/I_0 in different vacuums were obtained and were plotted in figure 3. A similar behaviour of the photocurrent's dependence on the ambient pressure, $I = I_0(3.69 - 0.87 \ln P)$, was also observed. These results indicated that the photocurrent still existed in the

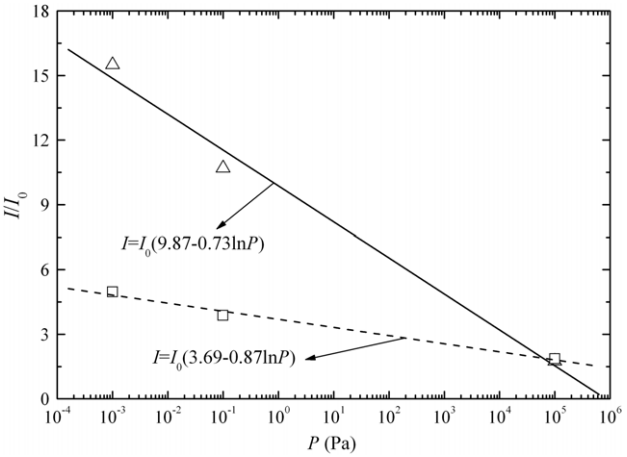

Figure 3. Photocurrent dependence of ambient pressure. The solid and dashed lines are logarithmic fits to the experimental data obtained from figure 2. The data denoted by open triangular and square symbols are the experimental results of initial cases in air and oxygen gases, respectively.

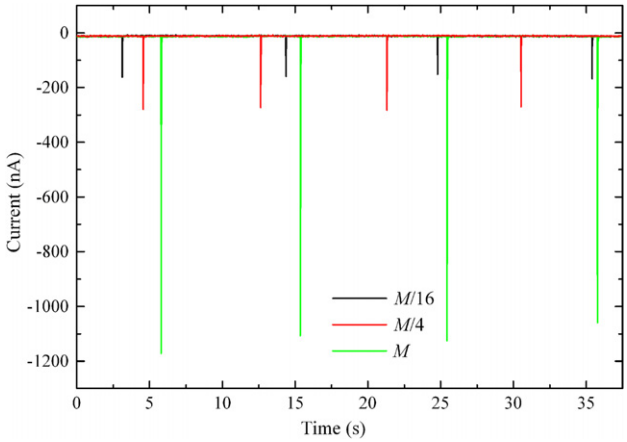

Figure 4. The dynamic characteristics of current with time and the effect of light intensity on the photocurrent of SWNT bundles measured at room temperature. The relaxation time (τ) is almost the same for different light intensity.

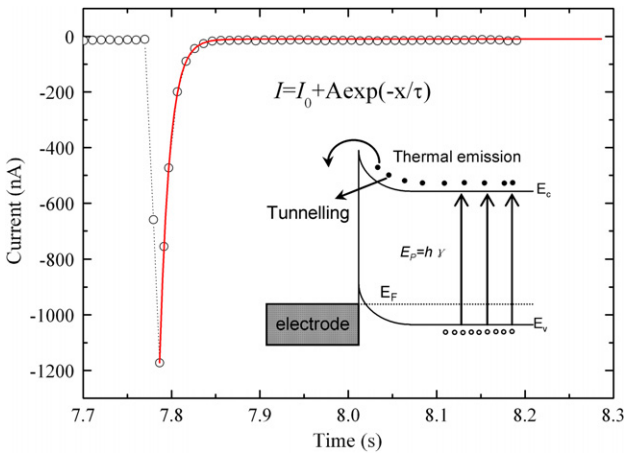

Figure 5. Typical dynamic response of photocurrent with time evolution. The red solid line represents the best exponential fit to the experimental data. The inset shows a schematic band diagram of Schottky barrier.

absence of gas molecules. In addition, it had an even higher amplitude than that in the presence of gas molecules, which implied that the gas molecular desorption mechanism [7,8,29] cannot be applied to interpret the observed photocurrent. The possible reason comes from the gas molecular inhibiting effects [18]. If gas molecules are present in the sample, they will bind onto SWNT surfaces and act as recombination centres or carrier traps, which facilitates the recombination of electrons and holes [10, 29]. Hence, the photocurrent generated in SWNTs in high vacuum has a larger value than that in low vacuum. When repeated on other samples, similar results were obtained. The above experiment signifies that the SWNT is sensitive to the ambient pressure, which permits it to be a promising pressure sensor.

We further investigated the photocurrent generated by different incident light intensities in a vacuum of $\sim 10^{-3}$ Pa. As displayed in figure 4, the photocurrent shows a prompt increase as the sample was illuminated. A close dependence of the photocurrent on the light intensity was observed. This result is in good agreement with the previous observations in single SWNT [16,30] and SWNT sheet [18], where the photocurrent was ascribed to the photoinduced charge carriers generation in SWNTs and subsequent charge separation across the metal–carbon nanotube contacts.

As discussed above, our experiments under different vacuums and different gas atmospheres implied that the gas molecular desorption mechanism is insufficient to explain the photocurrent generation. This can be further verified by analysing the dynamic process. Figure 5 shows the dynamic characteristics of the photocurrent of SWNT bundles during one light illumination. We find that the dynamic response of the photocurrent can be well described by the following dynamic model, $I = I_0 + A\exp(-t/\tau)$, where τ is the electron's lifetime. By fitting the experimental data with this formula, we find $\tau \sim 10$ ms which is much smaller than the typical time $\sim$10 s needed for gas molecular desorption [10, 17, 29] and 4.3 s for gas molecular photodesorption [8]. Considering the relaxation time τ depends strongly on numerous parameters, such as CNT sample structure (bundles, sheets, and single tubes, etc), sample preparation history, adsorbed gases and experimental setup, τ may be varies in a range of about an order of magnitude. Combining these two facts, the larger photocurrent generated under high vacuum and the shorter electron's lifetime, the gas molecular desorption mechanism cannot be applied to our experimental results.

To date, there are two main possible mechanisms for the experimentally observed photocurrent in CNTs. They are the gas desorption mechanism [7, 8] and the Schottky barrier existing at the metal–nanotube contacts [11–19], respectively. According to the above discussions, it is known that the gas desorption mechanism cannot interpret our experimental data. Therefore, we propose that the observed photocurrent comes from the Schottky barriers formed between the SWNTs and electrodes. Lu and Panchapakesan [18] and Lien *et al* [19] have found that the photocurrent directions can be altered by built-in potentials, which can be explained by the Schottky barriers. As shown in the inset of figure 5, once the carbon nanotubes

were illuminated, the energy of phonon was absorbed by the nanotubes, and the electron–hole pairs or excitons [7, 31] were subsequently generated. These carriers can move randomly in the nanotubes as no voltage was applied onto the sample. As these carriers arrive at the metal–nanotube contacts, some of them have the probability of getting across the Schottky barrier and arriving at the metal electrode via tunnelling or thermal emission process [18]. Once these electrons enter the metal, they will not recombine with the holes, thus the charge carrier separation takes place. It should be noted that thermal effects [18, 28, 32] due to light absorption has to be considered in this case, which is evidenced from the ignition of SWNTs when it is exposed to a conventional photographic flashlight [33]. The temperature rise generated by multi-phonon processes results in the increase in the electronic kinetic energy, which means the electrons have a higher probability of getting across the Schottky barrier, resulting in a larger photocurrent [34].

Finally, we compare the photocurrent generated in SWNT bundles with that in SWNT sheets. In previous studies [6, 18, 19], it has been found that the photocurrent shows a close dependence on the illumination position. The photocurrent has a maximum as the incident light illuminates the electrodes, and only a small photocurrent (a few per cent of dark current) can be observed if the whole nanotube samples were illuminated [18]. However, in our case, even when the whole sample is exposed to light illumination, a large photocurrent increasing from ∼17 nA to ∼30 nA (an increase of ∼2 times) can be seen in air. If it is illuminated in high vacuum, the photocurrent can increase by almost 20 times. This phenomenon should be related to with the sample's structure. In the SWNT sheet, the nanotubes are randomly aligned, while in SWNT bundles, the nanotubes are much better aligned, which can be seen from figure 1(*a*). Thus the carriers have a longer lifetime and higher possibility of getting across the Schottky barrier. Therefore, compared with the SWNT sheet, a much pronounced photocurrent can be generated in the SWNT bundles under the same measurement conditions.

4. Conclusions

In conclusion, we have demonstrated that SWNTs are able to generate a large photocurrent under a camera flash. The ambient pressure and the light intensity affect the photocurrent notably. The photon-induced electron–hole pairs in nanotubes and their subsequent separation across the Schottky barrier were responsible for the observed large photocurrent. The sensitivity of SWNTs to ambient pressure and light intensity makes them an ideal pressure sensor and photosensitive detector for practical applications.

Acknowledgments

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References

[1] Saito R, Dresselhaus G and Dresselhaus M S 1998 *Physical Properties of Carbon Nanotubes* (London: Imperial College Press)
[2] Misewich J A, Martel R, Avouris P, Tsang J C, Heinze S and Tersoff J 2003 *Science* **300** 783
[3] Wu Z C, Chen Z H, Du X, Logan J M, Sippel J, Nikolou M, Kamaras K, Reynolds J R, Tanner D B, Hebard A F and Rinzler A G 2004 *Science* **305** 1273
[4] Barone P W, Baik S, Heller D A and Strano M S 2005 *Nature Mater.* **4** 86
[5] Dresselhaus M S, Dresselhaus G and Avouris P 2001 *Carbon Nanotubes: Synthesis, Structure, Properties and Applications* vol 80 (Berlin: Springer)
[6] Zhang Y and Iijima S 1999 *Phys. Rev. Lett.* **82** 3472
[7] Fujiwara A, Matsuoka Y, Suematsu H, Ogawa N, Miyano K, Kataura H, Maniwa Y, Suzuki S and Achiba Y 2001 *Japan. J. Appl. Phys.* **40** L1229
[8] Levitsky I A and Euler W B 2003 *Appl. Phys. Lett.* **83** 1857
[9] Collins P G, Bradley K, Ishigami M and Zettl A 2000 *Science* **287** 1801
[10] Kong J, Franklin N R, Zhou C W, Chapline M G, Peng S, Cho K J and Dai H J 2000 *Science* **287** 622
[11] Tans S J, Verschueren A R M and Dekker C 1998 *Nature* **393** 49
[12] Martel R, Schmidt T, Shea H R, Hertel T and Avouris P 1998 *Appl. Phys. Lett.* **73** 2447
[13] Wind S J, Appenzeller J, Martel R, Derycke V and Avouris P 2002 *J. Vac. Sci. Technol.* B **20** 2798
[14] Javey A, Kim H, Brink M, Wang Q, Ural A, Guo J, McIntyre P, McEuen P, Lundstrom M and Dai H J 2002 *Nature Mater.* **1** 241
[15] Rosenblatt S, Yaish Y, Park J, Gore J, Sazonova V and McEuen P L 2002 *Nano Lett.* **2** 869
[16] Freitag M, Martin Y, Misewich J A, Martel R and Avouris P 2003 *Nano Lett.* **3** 1067
[17] Shim M and Siddons G P 2003 *Appl. Phys. Lett.* **83** 3564
[18] Lu S X and Panchapakesan B 2006 *Nanotechnology* **17** 1843
[19] Lien D H, Hsu W K, Zan H W, Tai N H and Tsai C H 2006 *Adv. Mater.* **18** 98
[20] Ando T 1997 *J. Phys. Soc. Japan* **66** 1066
[21] Spataru C D, Ismail-Beigi S, Benedict L X and Louie S G 2004 *Phys. Rev. Lett.* **92** 077402
[22] Perebeinos V, Tersoff J and Avouris Ph 2004 *Phys. Rev. Lett.* **92** 257402
[23] Sheng C X, Vardeny Z V, Dalton A B and Baughman R H 2005 *Phys. Rev.* B **71** 125427
[24] Wang F, Dukovic G, Brus L E and Heinz T F 2005 *Science* **308** 838
[25] Chen J, Perebeinos V, Freitag M, Tsang J, Fu Q, Liu J and Avouris P 2005 *Science* **310** 1171
[26] Song L *et al* 2004 *Adv. Mater.* **16** 1529
[27] Zhou Z P *et al* 2004 *J. Phys. Chem.* B **108** 10751
[28] Itkis M E, Borondics F, Yu A P and Haddon R C 2006 *Science* **312** 413
[29] Robert J C, Nathan R F, Jing K, Jien C, Thomas W T, Yuegang Z and Hongjie D 2001 *Appl. Phys. Lett.* **79** 2258
[30] Balasubramanian K, Fan Y W, Burghard M, Kern K, Friedrich M, Wannek U and Mews A 2004 *Appl. Phys. Lett.* **84** 2400
[31] Korovyanko O J, Sheng C X, Vardeny Z V, Dalton A B and Baughman R H 2004 *Phys. Rev. Lett.* **92** 017403
[32] Grigorian L, Sumanasekera G U, Loper A L, Fang S L, Allen J L and Eklund P C 1999 *Phys. Rev.* B **60** R11309
[33] Ajayan P M, Terrones M, de la Guardia A, Huc V, Grobert N, Wei B Q, Lezec H, Ramanath G and Ebbesen T W 2002 *Science* **296** 705
[34] Muller R S, Kamins T I and Chan M 2002 *Device Electronics for Integrated Circuits* (New York :Wiley)