Photoconductivity of single-wall carbon nanotubes under continuous-wave near-infrared illumination

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The photoconductivity of films of single-wall carbon nanotubes has been studied under continuous-wave near-infrared illumination. The photocurrent exhibits a linear response with the light intensity and with bias voltage up to 5 V. The temporal photoresponse of on/off step illumination shows a relatively slow relaxation time (4.3 s for films with a thickness of ~500 nm), which can be interpreted in terms of a kinetic model that takes into account the binding of photoelectrons with adsorbed oxygen. Possible applications of this photosensitive material are discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1606099]

The large amount of attention to electronic and optical properties of single-wall carbon nanotubes (SWNTs) is associated with both the nanotube’s well-defined one-dimensional (1D) structure and the possibility of employing them as building blocks for various nanotechnology applications. In particular, the interaction of light with the nanotube structures is a matter of special interest due to the opportunity to observe new photophysical effects related to nanotube low dimensionality and quantum confinement. For the past several years, numerous studies have been performed in the field of nanotube light absorption, fluorescence, Raman scattering, fluorescence, photoinduced molecular desorption, and nonlinear optical properties. Nevertheless, SWNT photoconductivity remains a practically unexplored area: a temporal photocurrent was detected in an earlier reported observation of SWNT mat photoconductivity using pulsed laser excitation. Such scarcity of information hints that observation of steady-state SWNT photoconductivity can be hampered by obstacles related to low light absorption of the nanotubes and/or a high level of dark current due to metal conductivity masking the semiconductor properties.

Thus, SWNT photoconductive response under steady-state or continuous-wave (cw) illumination is interesting not only for fundamental understanding of SWNT photoinduced processes, but also for the development of a new photosensitive material with unique optical and conductivity features. For example, the dependence of the nanotube band gap on its diameter enables easy tuning of the photodetector spectral range. In this letter, we report the observation of cw photoconductivity of single-wall carbon nanotubes in the near-infrared (NIR) spectral range.

SWNTs were synthesized by the arc discharge method and purified (85%) using air oxidation, acid treatment and thermal annealing, as purchased from BuckyUSA, Inc. The average diameter of the nanotubes was in the range of 0.8–1.1 nm according to NIR spectroscopy and transmission electron microscopy (TEM) observation. For the photoconductivity study, a nanotube suspension in methanol (0.8 mg/ml) was sonicated for about 30 min followed by dropping a small amount (2–3 μl) onto a patterned gold substrate with an insulating gap between the opposite electrodes [Fig. 1(a)]. The typical film thickness was 0.2–0.5 μm, except for specially prepared dense thick films (~10–15 μm) from a highly concentrated suspension. The gap width between electrodes was varied from 15 to 300 μm, and the sample resistance was in the range of 100–1500 Ω. The light source was a tungsten–halogen lamp with a long pass NIR filter (850 nm), enabling exposure of the SWNT samples in the region of their maximum NIR absorption that corresponds to the first principal transition (v→v') between Van Hove singularities of the density of states of semiconducting SWNTs [Fig. 1(b)]. The fine structure of the band (1000–1700 nm) was similar to that observed for SWNTs prepared by the HiPco process and there are at least four subbands, which can be assigned to the distribution of nanotubes with different diameters in the range of 0.8–1.1 nm. The integrated illumination power after the NIR filter was about 12 mW/mm². A Keithley-2000 multimeter (current meter) and Keithley-236 source-measure unit (voltage source and I–V measurements) were connected in a series with the tested sample. A Perkin-Elmer Lambda 900 spectrophotometer was used to record Vis-NIR absorption spectra.

The typical photocurrent response for several on/off light illumination cycles is shown in Fig. 2. Since SWNTs have their own low resistivity (~10⁻² Ω cm for as grown mat, for our samples the resistivity was in the range of 6–8 × 10⁻² Ω cm) it was important to carry out the current measurement with a high dynamical range. Therefore the Keithley-2000 (5.5 digits) was chosen to provide reliable detection of ~0.1 μA changes on a mA scale. The current increase cannot be explained by sample heating since a decrease of current would be observed. Indeed, direct heating (up to 80–100 °C) results in slow current reduction, which is consistent with similar (metallic) resistivity dependences on the temperature for SWNT mats. Two features in the photocurrent temporal behavior are of interest: a dark current drift and a relatively slow rise/decay (~4–5 s relaxation time) of the photocurrent in response to step on/off illumination.

For dark current density less than (1–1.5) × 10⁻¹³ A/cm² the background exhibits an increasing drift current over time. However, for higher values of current den-
The internal sample capacitance that forms a illumination cycle is not a result of the instrumental function. However, for higher current values, ohmic heating is responsible for the dark current in these results, we conclude that at relatively low current density the drift current decreases. This effect can be understood in terms of competition between two mechanisms that affect the SWNT conductivity: oxygen sorption and sample heating. It is known that carbon nanotubes in air possess conductivity, which is mostly due to oxidation by absorbed oxygen. Alternately exposing a sample to oxygen and nitrogen resulted in an increase (0.6%) and a decrease (0.1%) of the dark current from the initial value, respectively. Additionally, samples under illumination by a mercury lamp (12 μW/mm², integrated intensity) demonstrated a reduction of dark current, which is consistent with oxygen photodesorption induced by UV light from the SWNT surface. From these results, we conclude that at relatively low current density, oxygen sorption is responsible for the dark current increase. However, for higher current values, ohmic heating (SWNT/gold contact or SWNT intersections) likely becomes the dominant mechanism and leads to background reduction.

A photoinduced relaxation time (4–5 s) in the on/off illumination cycle is not a result of the instrumental function nor is the internal sample capacitance that forms a R–C circuit. Instrumental function was tested by switching between two resistors to simulate the resistance reduction in the SWNT sample under light exposure. A possible delay due to an internal R–C circuit was ruled out by measurement of the relaxation time for dark current using a step voltage. In both cases, the relaxation times were less than 0.5 s. The observed photoinduced relaxation can be interpreted in terms of a simple kinetic model by taking into account processes of photocarrier generation and relaxation. The rate equation for these processes is given as

\[ \frac{dn}{dt} = \eta I - (k_a + k_t)n - \gamma n^2, \]

where \( n \) is the concentration of photocarriers, proportional to the photocurrent; \( I \) is the intensity of the incident light; \( \eta \) is the rate of charge generation; \( k_a \) is the rate for annihilation of carriers at the electrodes; \( k_t \) is the rate for carrier trapping by deep traps or carrier localization; and \( \gamma \) is the rate of bimolecular recombination. At steady-state excitation \( \left( \frac{dn}{dt} = 0 \right) \), two limits exist: \( n \sim I / \eta \), when \( k_a + k_t > \gamma \) and \( n \sim I^{1/2} \), when \( k_a + k_t < \gamma \). The dependence of the photocurrent on the incident light intensity demonstrates the linear character of SWNT films [Fig. 3(a)]. This is in agreement with the above considered oxidation process: photogenerated electrons are captured by oxygen and remaining photoholes become major photocarriers, thereby reducing the probability of a recombination process. For this limit, the temporal photocurrent behavior on step illumination can be described by an exponential function,

\[ n(t) = \frac{n_I}{k_a + k_t}(1 - e^{-(k_a + k_t)t}). \]

Indeed the photocurrent rise is fitted well by the exponential function as is seen in Fig. 3(b).

We did not find any dependence on the gap width of the photoinduced relaxation time, \( \tau = (k_a + k_t)^{-1} \). Samples with interelectrode gap widths of 15, 50, 70, 200, and 300 μm were tested. For a gap width of 5 μm it was difficult to reliably detect the photocurrent because of the low sample resistance and the small surface area absorbing the light. Sample width of 5 μm and less is interesting because in this case the nanotube length is comparable to the interelectrode distance. The average \( \tau \) value (eight samples) is 4.3 ± 0.3 s.
The absence of $\tau$ dependence on the gap between the electrodes indicates that the rate of carrier annihilation at the electrodes, $k_{a}$, is small and that $\tau$ is mainly defined by the trapping process, $k_{t}$. The nature of the carrier trapping and/or localization could be associated with SWNT intersections and/or an oxidation process. It was shown recently\textsuperscript{13} that the intersection between metallic and semiconducting SWNTs forms a Schottky barrier with height about one half of the band gap of a semiconducting SWNT. Also, the concentration of defects in the vicinity of nanotube intersection (individual and bundle) should be higher than for remote areas. However, the characteristic times for charge trapping/localization at intersection areas should be much shorter than the experimental values observed. A rough estimate gives these values on a subnanosecond scale: for classic transport ($L \gg L_{m}$, where $L$ and $L_{m}$ are the nanotube length and free path, respectively), the characteristic trapping rate, $k_{t} = CV_{F}/L_{m} \gg CV_{F}/L$, where $C$ is the linear concentration of defects/traps (intersections in this case) and $V_{F}$ is the Fermi velocity. Taking $V_{F} = 8 \times 10^{5}$ m/s, $C \approx (10^{-11} - 1) \mu m^{-1}$ from the AFM image, Fig. 1(a), and $L \approx 5 \mu m$, we can get an estimated time of $\tau = k_{t}^{-1} \approx 10^{-10} - 10^{-11}$ s. Therefore, we believe that the most reasonable explanation is related to photoelectron-oxygen binding. An indication of that is the similarity in photoconductive relaxation time with the rise time of current under oxygen exposure ($\approx 10$ s). Strictly speaking, this value consists of the average $O_{2}$ diffusion time inside the film and the characteristic $O_{2}$–SWNT binding time, which defines the photoconductive relaxation. As was reported previously,\textsuperscript{14} the characteristic time for individual SWNT (where a gas diffusion process can be excluded) exposed to $NO_{2}$ (oxidizer) is tens of seconds, an order of magnitude that is consistent with our results. Another confirmation of the proposed model is the increase of the photoconductive relaxation (up to $8 - 10$ s) for thick dense SWNT films ($10 - 15 \mu m$) as a result of the lower $O_{2}$ concentration absorbed at the bulk compared to the surface.

The photocurrent exhibits a linear dependence on the bias applied (up to 5 V), and no threshold is observed at low voltage, when the signal value is compared with the noise level. This observation neither supports nor refutes the proposed model.

In conclusion, it was demonstrated that single-wall carbon nanotubes are capable of absorbing cw NIR light and generating a photocurrent under low applied bias. This phenomenon can be employed to develop a NIR photodetector based on the unique photophysical properties of carbon nanotubes:\textsuperscript{15} low-noise level due to reduced electron-phonon coupling in 1D systems, the possibility to easily tune the band gap by varying the nanotube diameter, and field-effect dark current suppression.\textsuperscript{15}

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