Photoelectronic transport imaging of individual semiconducting carbon nanotubes

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Photoconductivity in individual semiconducting single-wall carbon nanotubes was investigated using a confocal scanning optical microscope. The magnitude of the photocurrent was found to increase linearly with the laser intensity, and to be maximum for parallel orientation between the light polarization and the tube axis. Larger currents were obtained upon illuminating the tubes at 514.5 nm in comparison to those at 647.1 nm, consistent with the semiconducting tubes having a resonant absorption energy at the former wavelength. Moreover, the determination of the photoresponse as a function of position along single nanotubes has proven to be a useful tool to monitor local electronic structure effects. © *2004 American Institute of Physics.*
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Single-wall carbon nanotubes (SWCNTs) are promising components of nano-scale electronic devices.[1] While the electrical properties of SWCNTs have been thoroughly investigated in the dark,[2] much less is known about their photoconductive behavior. Thin SWCNT films have been shown to exhibit photoconductivity.[3] Most recently, infrared photoconductivity has been measured on individual semiconducting SWCNTs[4] acting as channels in ambipolar field-effect transistors (FETs). The observed phenomena are in accordance with the presence of Schottky barriers at the metal contacts,[5] which is well documented from studies on the operation mechanism of tube FETs.[6,7] However, no direct evidence for the role of these barriers was obtained due to the fact that the whole sample was illuminated. In this letter, we report on measurements capable of spatially separating the photocurrent contributions from different regions along single SWCNTs.

SWCNTs (Carbolex® arc-discharge material) were deposited on an $n+$-silicon substrate, suitable as back gate, with a 100 nm thermally grown SiO_2 layer. After e-beam lithography, electrodes were deposited by evaporating 0.5 nm Ti/15 nm AuPd on top of the nanotubes. Figure 1(a) shows the atomic force microscope (AFM) image of one of the fabricated FETs with a single SWCNT ($\approx 1.3 \pm 0.3$ nm in height) contacted between two electrodes $\approx 1.5\ \mu$m apart. Electrical measurements were carried out at room temperature, in most cases under ambient conditions. Initially, the SWCNTs were identified as metallic or semiconducting according to their gate dependence of conductance.[2] The ten different semiconducting devices investigated in this work exhibited p-type behavior with an ON/OFF current ratio exceeding 10^3 in the gate voltage range of ± 5 V. Due to the presence of humidity, the conductance versus gate voltage curves exhibited pronounced hysteresis.[8] Before starting the photoconductivity experiments, the FETs were switched to the OFF state by performing one full gate voltage cycle[9] [see, e.g., Fig. 1(b)]. This state was found to be stable under the conditions of subsequent measurements.

A confocal scanning microscope was used to locally illuminate this sample by a diffraction-limited laser spot (300–400 nm diameter) as described previously for recording Raman images of isolated SWCNTs.[10] Figure 1(c) shows a Raman image of the G-line intensity, acquired at an excitation wavelength of 514.5 nm with a laser intensity of

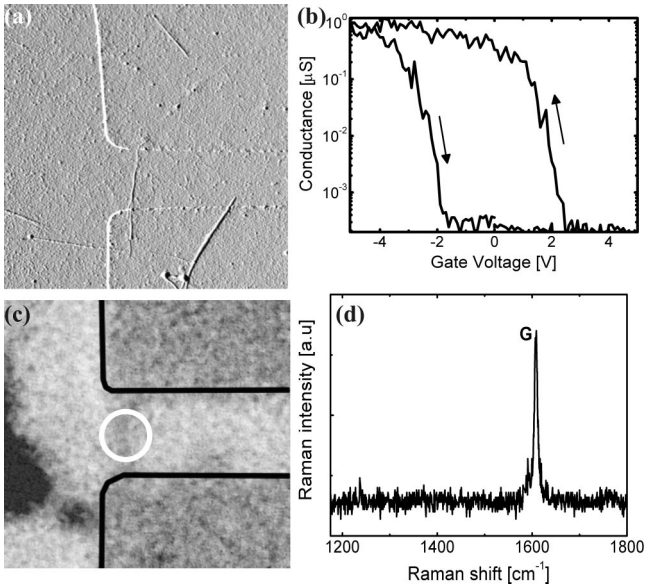

FIG. 1. (a) AFM amplitude image of a FET comprising one semiconducting SWCNT (height $\approx 1.3 \pm 0.3$ nm). The gap between the electrodes is $\approx 1.5\ \mu$m, and the size of the image is $5 \times 5\ \mu$m^2. (b) Gate dependence of conductivity for the same sample with a drain–source voltage of 0.1 V. The arrows indicate the direction in which the gate voltage is scanned. (c) False color Raman G-line image of the sample ($\lambda = 514.5$ nm, 0.5 MW/cm^2), overlaid with a reflection image to obtain the position of electrodes. (d) Raman spectrum of the contacted SWCNT taken with the laser spot ($\lambda = 514.5$ nm, 0.5 MW/cm^2) positioned at the marked region (circle) in the Raman image of (c). The intense peak at ≈ 1590 cm^{-1} corresponds to the tangential mode (G line) in a semiconducting SWCNT.

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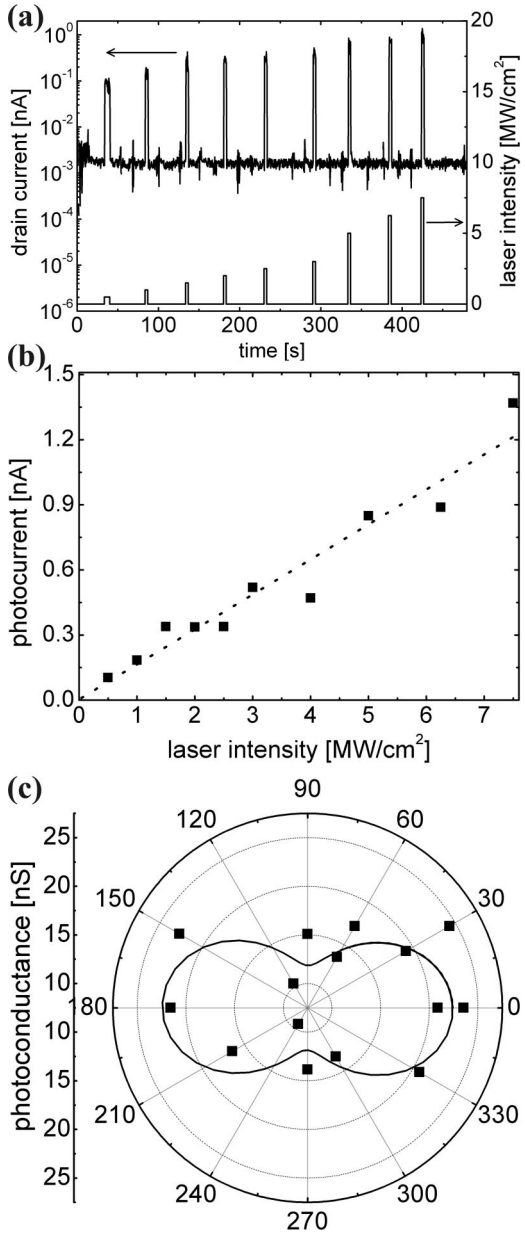

FIG. 2. (a) Room temperature currents (plotted in log scale) measured on a single SWCNT ($V_{bias}=0.1$ V) upon illumination with various laser intensities ($\lambda=514.5$ nm) and pulse widths of 3 or 7 s. (b) Dependence of the photogenerated current in (a) plotted as a function of laser intensity. The dotted straight line is a linear fit to the measured data. (c) Polarization dependence of the photoconductance of a single SWCNT under illumination with $\lambda=514.5$ nm ($V_{bias}=0.1$ V).

0.5 MW/cm^2, which is overlaid over a reflection image of the same substrate area. In addition to the gate dependence shown in Fig. 1(b) the Raman spectrum of the contacted SWCNT presented in Fig. 1(d) signifies that this tube is semiconducting, as is apparent from the absence of the Breit–Wigner–Fano line characteristic of metallic SWCNTs.[11]

By using such a combination of Raman and reflection images the photocurrent through a single SWCNT can be detected by positioning the laser spot over the tube in the electrode gap. As shown in Fig. 2(a), a pronounced increase in current was observed upon illumination with $\lambda=514.5$ nm and laser intensities varying from 0.5 to 7.5 MW/cm^2. The plot shown in Fig. 2(b) displays a linear dependence of the photocurrent measured at different laser intensities. This is in agreement with the earlier observation on single SWCNTs,[4] indicating that photogenerated charge carriers in the nanotube are responsible for the current increase. Noteworthy are the laser intensities used in the present work that fall into the range of 0.5–7.5 MW/cm^2, which is approximately three orders of magnitude larger than in Ref. 4. At such high laser intensities (and small bias voltages $\leqslant 0.1$ V), no alteration in photocurrent was observed when the environment was changed from air to argon, oxygen, or water vapor. This result suggests that the photocurrent does not result from photodesorption[12] of adsorbates like oxygen[13,14] and water,[8] which have been reported to affect the electrical transport properties of semiconducting SWCNTs. Furthermore, the photocurrents were one order of magnitude smaller when the samples were illuminated by $\lambda=647.1$ nm, as compared to excitation with $\lambda=514.5$ nm with the same laser intensity (0.5 MW/cm^2). This difference is expected since the absorption cross section of the semiconducting nanotubes is much higher at 514.5 nm. In particular, the semiconducting interband transitions corresponding to the third van Hove singularities fall close to 2.41 eV for the samples used here,[15] which have a mean diameter of ≈ 1.3 nm.

To gain additional support that optically excited charge carriers in the SWCNT are the origin of the current changes observed under illumination, the dependence of photocurrent on the polarization direction of the incident light was studied. The polar plot in Fig. 2(c) illustrates the result of such a measurement, where 0° corresponds to the direction of polarization being parallel to the nanotube axis. It shows a clear dependence of the photoconductance on the orientation of the nanotube. For the present sample, a polarization ratio of approximately 5:1 is found. The polarization dependence of the photoconductance excludes that photovoltages created at the $n+$-Si/SiO$_2$ interface are responsible for the current changes upon laser illumination.

The relatively small extension of the laser spot (300–400 nm), as compared to the separation of the electrodes ($\approx 1.5\ \mu$m), opens up the possibility to record the photocurrent signal that originates from illumination at different locations along a contacted SWCNT. Such a photoelectronic transport image is depicted in Fig. 3 In order to highlight the electrode positions, the photocurrent image was overlaid above a simultaneously taken reflection image. It is apparent that the magnitude of the photocurrent is strongest closest to the top electrode. This observation is attributed to the generation of an offset photovoltage upon illumination of the Schottky barrier at the contact region.[16] With increasing distance from the contact, the flat band region is reached where the major effect is photogeneration of carriers that experience a much weaker field. Similar observations have been made also on the other samples. The absence of a corresponding photocurrent peak close to the other electrode may be explained by an asymmetry in the Schottky barriers at the source and the drain.[6]

In conclusion, we have presented a versatile approach to investigate individual nanowires by recording photoconductivity and Raman spectra on the same electrically contacted semiconducting SWCNTs. Due to its local probe character,

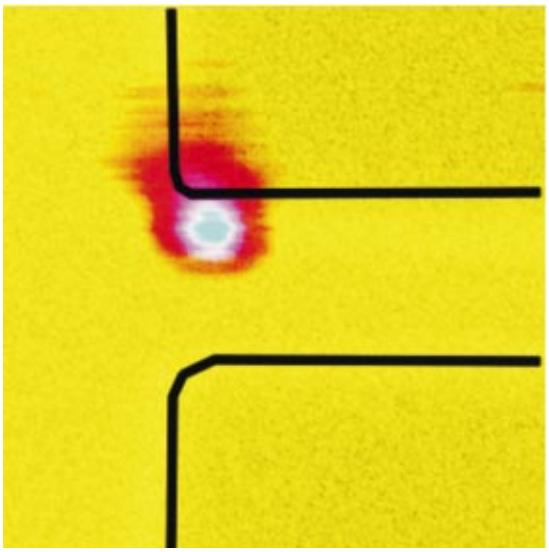

FIG. 3. (Color) Photoelectronic transport image of the sample in Fig. 1 with a bias voltage of 0.1 V ($0.5\ \mathrm{MW/cm^2}$ at $\lambda = 514.5$ nm). A reflection image of the sample taken simultaneously has been superposed to obtain the approximate position of the electrodes, which are shown as black lines. A maximum photocurrent of 0.11 nA is observed at the bright spot close to the electrode. The current is a maximum at the cyan colored region and goes gradually down to a minimum in the yellow colored region.

this method reveals significant photovoltage generation close to the nanotube–electrode contact, which was absent upon illumination of the tube body. Future experiments addressing the effects of bias polarity, gate potential, and contact configuration are expected to provide useful new insights into the local photoelectronic properties of carbon nanotubes.

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