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Citation for published version (APA):

Freitag, M., Tsang, J. C., Bol, A., Avouris, P., Yuan, D., & Liu, J. (2007). Scanning photovoltage microscopy of potential modulations in carbon nanotubes. *Applied Physics Letters*, 91(3), [031101].
<https://doi.org/10.1063/1.2757100>

DOI:

[10.1063/1.2757100](https://doi.org/10.1063/1.2757100)

Document status and date:

Published: 01/08/2007

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Citation: *Appl. Phys. Lett.* **91**, 031101 (2007); doi: 10.1063/1.2757100

View online: <https://doi.org/10.1063/1.2757100>

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Scanning photovoltage microscopy of potential modulations in carbon nanotubes

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(Received 14 May 2007; accepted 19 June 2007; published online 16 July 2007)

We use the locally generated photovoltage in carbon nanotubes to image potential modulations produced by defects. The correlation with spatially resolved spectroscopy of the disorder-enhanced Raman band allows us to locate the defects and to determine their effect on band bending. The defects produce local potential maxima, which are consistent with trapped electrons near the tube. An offset photovoltage is generated when the laser populates metastable traps in the oxide. Previously uncharged defects can thus be imaged. To demonstrate the versatility of the technique, we show that tube-tube junction at the base of nanotube loops can be electronically characterized.

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Carbon nanotubes (CNTs) are strong and seamless cylinders of sp^2 -hybridized carbon, ideally suited for nanoscale electronics.¹ The environment in which nanotubes are placed to form carbon nanotube field-effect transistors (CNTFETs), however, is not ideal. In particular, the gate oxide has charge traps both at the surface and in the bulk, which affect the conduction through the CNT and lead to a hysteresis.^{2–4} Adsorbents that locally dope the CNT will usually be present as well. These environmental effects are common in real-world CNTFETs and it is necessary to understand their role in active devices. Here we use scanning photovoltage microscopy to probe the built-in potentials in the CNT that are associated with defects. Disorder is independently measured by spatially resolved Raman spectroscopy of the D band. The two characterization techniques are shown to be sensitive to the same defects. Initially unpopulated shallow traps near the tube are also populated by the laser light. Scanning the laser laterally produces a moving potential step that is capable of inducing a photovoltage from the CNT. This effect can be used to generate image contrast in laser scanning microscopy of contacted one-dimensional structures that lack built-in fields. We apply it to CNT loops whose tube-tube contact can now be characterized without requiring four probes on the CNT⁵ or performing difficult measurements such as scanning superconducting quantum interference device microscopy.⁶

Carbon nanotubes were grown on silicon wafers with 100 or 200 nm SiO_2 . Up to 10 μm long and 1–2 nm wide tubes were grown from 3–4 nm iron oxide nanoparticles by ethanol chemical-vapor deposition. The recipe was otherwise similar to Ref. 7. Up to several 100 μm long CNTs with diameters around 2–3 nm were grown in a different setup from Fe/Mo nanoparticles.⁸ The feeding gases were CH_4 , C_2H_4 , and H_2 . Contacts are formed by e-beam lithography and evaporation of 7 Å Ti and 30 nm Pd. The degenerate silicon substrate is used as a backgate. The Raman/laser-scanning microscope utilizes a 100×0.8 NA objective and laser lines of 514.5 and 457.9 nm. Raman scattered light is filtered by a notch filter and analyzed in a 0.5 m single spec-

trometer with a 1200 lines/mm grating and a liquid-nitrogen cooled silicon charge-coupled device detector array. The sample is scanned with nanometer precision under the focused laser spot to record images of the scattered light, the Raman lines, and the photovoltage.

Scanning photovoltage microscopy is a useful probe for the potential gradients in one-dimensional devices. In the absence of an external bias, it is only the internal fields, such as the ones associated with Schottky barriers,^{9,10} p - n junctions,¹¹ or defects^{12–15} that can separate the photogenerated carriers and produce a photovoltage. An ideal CNTFET consists of two back-to-back Schottky barriers at the source and drain contacts and a flatband region in the middle of the device. Figure 1(a) shows a short-circuit photocurrent (I_{SC}) image of such a device taken with a focused laser spot of about 400 nm. The Schottky barriers always appear as two regions with opposite signs of I_{SC} because the potential gradients associated with the Schottky barriers are opposed.^{10,16} The interior of the CNT generates very little short-circuit photocurrent because the bands are flat there.

After this measurement, a single defect was created or populated in the CNTFET by positioning the focused laser spot with ~ 600 μW of power in the center of the device for 5 min. It is highly unlikely that an intrinsic defect in the CNT can be created at such low power levels and photon energies. Typical increases in temperature as measured by Raman Stokes/anti-Stokes ratios are only a few degrees. CNTs are oxidized at much higher temperatures of around 700 °C, which means that the defect is most likely preexisting in the silicon oxide, or on the surface, and we change its charge state. With a localized defect in an otherwise pristine device, we can determine the photovoltage contrast that such a defect will produce in I_{SC} images and use this result later in more complicated situations with multiple defects.

The defect in Fig. 1(b) appears as two adjacent spots, one with a positive sign and another with a negative sign of I_{SC} . This contrast can be explained for a local potential extreme with two regions of opposite potential gradient to the left and right [Fig. 1(d)]. Note that we measured I_{SC} with a preamplifier at the right electrode and a negative current means that holes travel to the right. Thus the pattern is only

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FIG. 1. (Color online) Short-circuit photocurrent microscopy of a pristine CNTFET with one introduced defect ($\lambda=457.9$ nm). (a) I_{SC} image of the initial CNTFET without defects. The pattern at the contacts is due to the Schottky barriers ($V_G=0$ V). (b) I_{SC} image of the same CNTFET with one defect in the middle ($V_G=0$ V). (c) I_{SC} image of the same CNTFET at $V_G=-25$ V. (This image was taken with chopped laser light and lock-in detection.) [(d) and (e)] Schematic illustration of the band bending under the conditions of (b) and (c).

consistent with a potential maximum and not a minimum, which means that electrons are trapped at the defect site. In general, both electron and hole traps can exist in silicon oxide and the spatially resolved photovoltage measurement can be used to tell which ones are active in a particular case. Figure 1(c) shows that the population of *this trap* could be inverted by applying a more negative backgate voltage (-25 V instead of 0 V). Under these conditions electrons tunnel from the trap to the CNT and the trap becomes positively charged.

Figure 2 shows data from a different CNTFET that is $7\ \mu\text{m}$ long and has multiple strong defects along its length as is apparent from its I_{SC} image [Fig. 2(a)]. The CNT did also show intense Raman features for excitation at $\lambda=514.5$ nm. Most importantly, the *D* band was observable and nonuniform along the tube length [Fig. 2(b)]. The presence of a Raman *D* band is usually attributed to disorder, because the associated phonon mode is located at the zone boundary, and first-order Raman spectroscopy is only sensitive to phonons with small momentum that are located close to the Γ point. However, elastic scattering induced by disorder can make this mode Raman active.¹⁷

Since photovoltage microscopy and Raman spectroscopy are both understood to probe disorder, it is important to ask whether the two methods probe the same kinds of defects. A comparison [dashed lines between panels (a) and (b)] suggests that there may be a correlation that is, however, 90° out

FIG. 2. (Color online) Short-circuit photocurrent microscopy and spatially resolved Raman scattering on the same CNT ($\lambda=514.5$ nm). (a) I_{SC} image of the CNTFET. (b) Raman image of the *D* band as a function of position along the CNT. (c) Integrated photocurrent signal along the CNT, used to reconstruct the band bending in the CNT. The band gap and Schottky barrier height are arbitrarily assigned. E_F is the Fermi level. E_C and E_V are the energies of the conduction and valence bands. Dashed lines are a guide to the eye and correlate the local potential maxima with strong *D*-band sites on the CNT.

of phase. The assumption that I_{SC} is proportional to the local potential *gradient* suggests that we should integrate I_{SC} along the CNT in order to reproduce the internal potential profile and band structure [Fig. 2(c)]. This method has been used before to extract energy-band profiles in silicon nanowires.¹⁸ Indeed, we find an almost perfect correlation between the photovoltage-derived band structure [Fig. 2(c)] and the Raman *D*-band intensity [Fig. 2(b)].¹⁹ Each local potential maximum coincides with a peak in Raman *D*-band intensity and the three highest potential maxima correspond to the three strongest Raman signals. Photocurrent imaging can therefore be used as an alternative to local Raman spectroscopy of the *D* band, which in practice is limited to CNTs that have a strong resonance enhancement.

If the simple picture of I_{SC} being proportional to the potential gradient were to hold universally, unbiased devices should exhibit both positive and negative regions in equal proportions. This is roughly the case for the device in Fig. 2 with strongly scattering defects, but in general, we often see large regions of CNTs that have an overall negative I_{SC} and at other times we see large regions that generate mainly positive I_{SC} . Even more interestingly, in those cases the sign depends on the scanning direction of the laser spot across the device. Figure 3 shows a CNT that lies on the substrate in the shape of a loop rather than a straight line. The two images in

FIG. 3. (Color online) Effect of an environmental potential step on the short-circuit photocurrent. (a) I_{SC} image of a looped CNT (30 μm source-drain distance). Large regions of an overall negative photoresponse alternate with regions of positive photoresponse. (b) I_{SC} image of the same CNTFET taken with a different scanning direction. [(c) and (d)] Sketch of the sign of the I_{SC} offset in (a) and (b). (e) Line scans along the lines indicated in (a) and (b). The defect-related signal is the same in both scans, but it has a negative offset in (a) and a positive offset in (b). (f) Schematic of the band bending as the environmental potential step is placed in the middle of the device. (g) I_{SC} image of a different CNTFET with strongly coupled tubes at the base of the loop (arrow). The inset shows a scanning electron microscopy image of the device.

Figs. 3(a) and 3(b) are taken under 90° rotated scanning directions of the laser spot that rasters the image line by line along the fast scan direction as indicated. Note that the sign of I_{SC} at the Schottky contacts stays the same and the strongly varying signal related to individual defects is preserved, but there is an overall positive or negative offset [Fig. 3(e)].

The offset can be explained when we assume that the laser is populating metastable traps with a net negative charge in our substrates.²⁰ By scanning part of the image, a region of the oxide is charged negatively and the rest is neutral (or less charged than the recently scanned region). This produces an electric field at the boundary between already scanned and pristine regions that can induce a photovoltage when light is incident on the CNT during the next scanned line [Fig. 3(f)]. The boundary moves along as the entire image is assembled, which gives the illusion that there is a built-in field pointing in the same direction along the entire CNT. In Fig. 3, the CNT is not straight, and there are regions where the electric field at the boundary points from source to drain and others where it points from drain to source. This explains the alternating pattern of positive and negative regions of offset voltage [Figs. 3(c) and 3(d)]. It is quite apparent that the fast scan direction has much less effect on the pattern than the slow scan direction, which means that the lifetime of the charged traps is much longer than the few seconds it takes to scan a line.

Figures 3(a) and 3(b) are both taken on CNTFETs with a loop and it is surprising that their I_{SC} images look so different. In Fig. 3(a), the photovoltage generated along the loop and along the rest of the CNTs are qualitatively similar, while in Fig. 3(g), the signal along the loop is by a factor of 20 weaker. This suggests in Fig. 3(a) a very weak tube-tube coupling at the base of the loop, while in Fig. 3(g) the photovoltage generated along the loop is essentially short cir-

cuted at the base. We have previously observed analogous variations of the base of loops in electrically induced infrared emission experiments with CNTFETs.⁶ Some CNTFETs did show light emission from loop bases under a unipolar current, while others did not. We suspect that in both the photocurrent and light emission measurements the difference can be attributed to the exact way the CNTs cross over each other, i.e., to what extent the carbon lattices are commensurate.²¹ Since light emission measurements probe the junctions at high voltages in excess of 10 V, and photovoltage microscopy probes the zero-bias behavior, the two techniques complement each other.

In conclusion, we have used the locally generated photovoltage of a CNTFET to image and understand the built-in potential modulations. The technique is applied to a device with a single defect, which produces a dipole-like contrast. From this and the correlation with spatial images of the Raman disorder band, we can understand the pattern produced by more complicated devices with many defects. We find that the laser light can also produce metastable potential steps along a device, which allows imaging of defect-free CNTs, but has to be taken into account generally for the interpretation of photovoltage images. Finally, we apply the technique to carbon nanotubes with loops, whose tube-tube junction at the base can now be characterized in the low-bias regime.

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¹⁹A small photocurrent offset has been added to the raw data before the integration was performed to make sure that the potential at the two contacts is identical. This procedure is justified by the need to correct metastable charges that are induced by the laser, as we discuss later. The height of the Schottky barrier and the size of the band gap have been arbitrarily assigned in the figure.

²⁰For trapped holes the pattern would be reversed.

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