

Supplementary Information for:

Optically Controlled Dielectric Properties of Single-
Walled Carbon Nanotubes for Terahertz Wave
Applications

Serguei Smirnov,^a Ilya V. Anoshkin,^{ab} Petr Demchenko,^b Daniel Gomon,^b

*Dmitri V. Lioubtchenko,^{*ab} Mikhail Khodzitsky,^b Joachim Oberhammer^a*

^aDepartment of Micro and Nanosystems, KTH Royal Institute of Technology,
Osqualdas väg 10, SE-100 44, Stockholm, Sweden

^bDepartment of Photonics and Optical Information Technologies, ITMO University,
49 Kronverkskiy pr., 197101, Saint Petersburg, Russian Federation

*E-mail: dml@kth.se

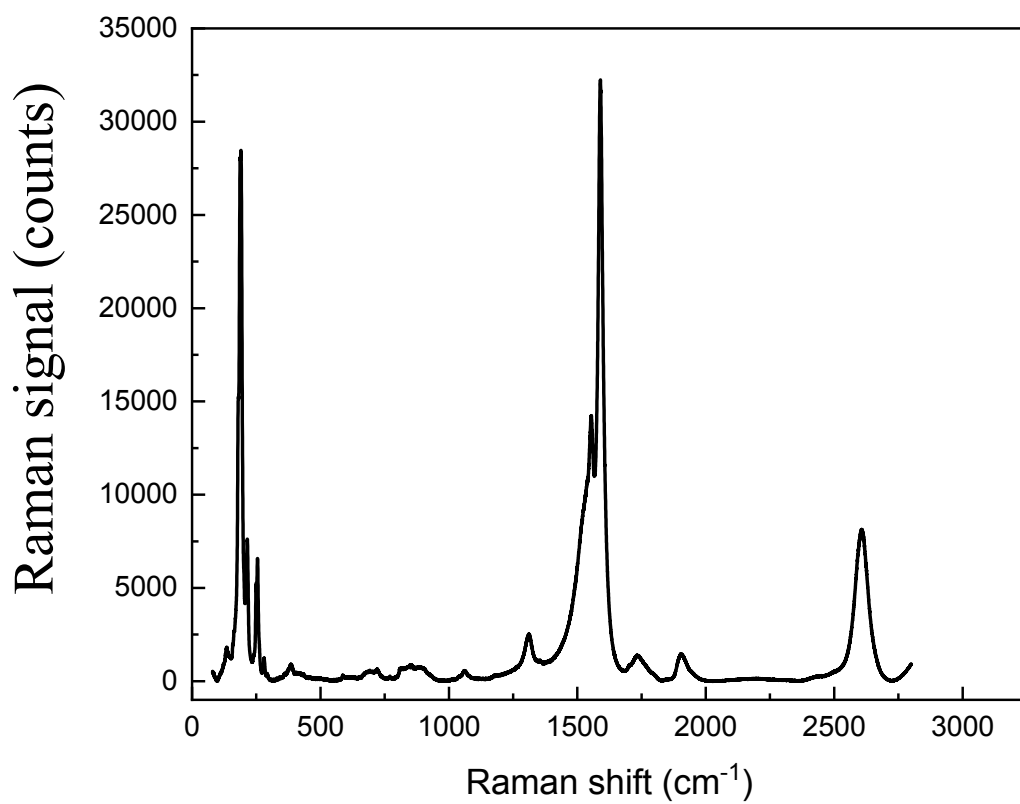


Fig. S1. Raman spectra of the SWCNT samples.

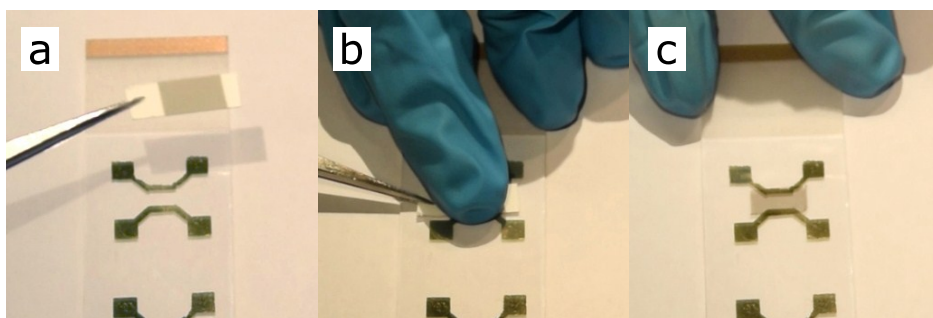


Fig. S2. Dry transfer method steps of the SWCNT layer onto a quartz substrate.

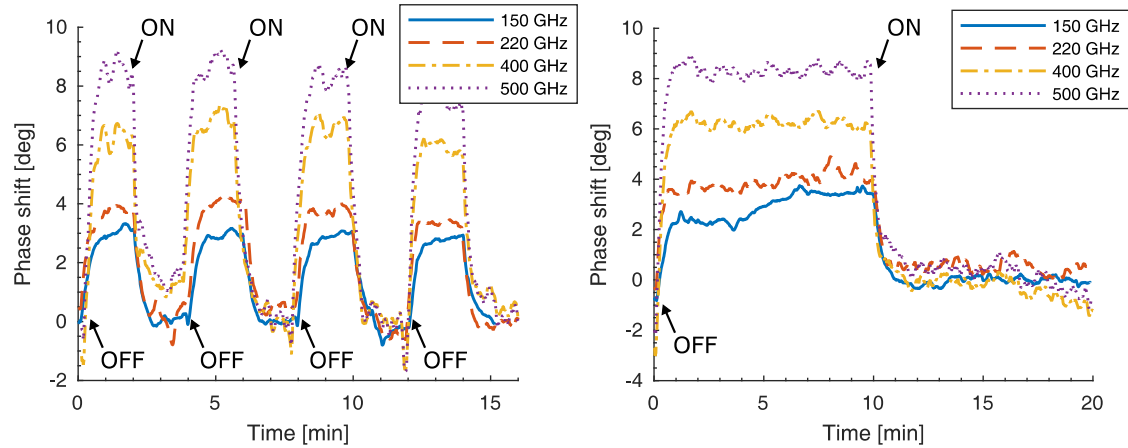


Fig. S3. Time dependence of the phase shift in the SWCNT-loaded DRW with 4 and 20 minutes on/off illumination cycles.

Methods

Carbon nanotube sample characterization: The SWCNT layers were characterized with a Perkin Elmer UV-vis-NIR spectrophotometer in the 200–2500 nm wavelength range. The optical spectrum was measured with a double beam spectrometer for the solid SWCNT layer on quartz substrate without liquid treatment. The presence of the strong peak at 280 nm corresponds to the π -plasmon with a long tail up to the IR range. The electronic transitions of the SWCNTs are overlapping with the tail of the π -plasmon, and the impurities give an additional baseline [1, 2]. The optical absorbance (A) of the SWCNT layer was derived from the transmission (T) measurements as [3]:

$$A = \log_{10}(100/T)$$

Scanning and transmission electron microscopy studies were done with high-resolution scanning electron microscope JEOL JSM-7500FA at 2 kV and 2.5 mm working distance, and spherical aberration corrected transmission electron microscope JEOL JEM-2200FS at 80 kV.

The purity of the SWCNT samples was controlled with TEM, Raman spectroscopy, thermogravimetric analysis, and calibrated EDX/SEM. Chemical composition of CNTs pristine and decorated with Ba^{2+} ions was used to estimate the oxygen containing groups and defects [4]. For this purpose, SWCNTs were immersed in a freshly membrane-filtered $\text{Ba}(\text{OH})_2$ water solution in DI Millipore water in CO_2 -free atmosphere followed by water washing to remove residual Ba^{2+}

ions. The chemical composition of SWCNTs after reaction with $\text{Ba}(\text{OH})_2$ was measured with calibrated EDX spectroscopy:

Atomic ratio:	C/Ba	O/Ba	C/O	C/Fe
	8620	436	19.8	9.18

The corresponding chemical composition for SWCNTs is $\text{C}_{400}\text{O}_{32,1}(\text{COOH})_2$ and the concentration of Fe admixtures is 9.4 % (at.). All Fe nanoparticles were found to be encapsulated inside SWCNTs/carbon shell and do not influence the optical properties [4].

Raman spectroscopy shows all carbon atoms, incorporated in the SWCNT structure and in the impurities. The quantity of nontubular impurities can be determined by the D/G peaks ratio. According to our results the D/G ratio is 0.075 (see Fig. S1) which means that amount of the admixture of nontubular carbon forms is very low.

Capacitance and resistance measurements were carried out with an Agilent B1500A semiconductor device analyzer at 1 MHz

THz TDS measurement setup: The femtosecond IR laser parameters were the following: a central wavelength of 1040 nm; a full width at half maximum of 5 nm; an average output power of 1.1 W; and a pulse width of 120 fs. The optical path of the “pump beam” was controlled with an optical delay line and modulated with a chopper at 667 Hz. The THz radiation induced birefringence in the electro-optical crystal (CdTe) for the “probe beam”. The Wollaston prism (W) split the “probe beam” into two beams with orthogonal polarizations, which were detected by balanced photodiodes. For the peak amplitude measurement, the integration time of the lock-in-amplifier was increased up to 1 second to increase the accuracy. The delay line was set corresponding to the maximum of the pulse amplitude (~5.3 ps) (inset in Fig. 2b).

The real part of the dielectric constant of high-resistivity silicon with thickness of 1052 μm was measured by our TDS setup and by Dai et al in [5], see Fig. 4.

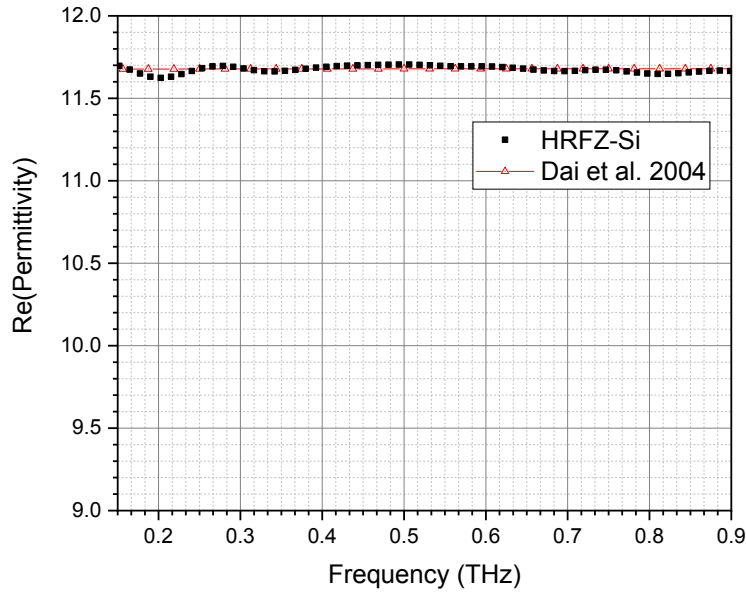


Fig. S4. The real part of the dielectric constant of 1052 μm thick high resistivity silicon measured by TDS setup and by measured in [5].

THZ VNA measurement setup: A sapphire DRW was mechanically supported by a rigid Rohacell foam structure with a low dielectric constant and low loss tangent. Sapphire was chosen as a pure dielectric, transparent in the wide range of the visible and near-infrared light spectrum. The cross-section dimensions of $1.0 \times 0.5 \text{ mm}^2$ and the 6 mm-long tapers, symmetrical in the E -plane, were chosen according to the work of Lioubtchenko et al. [6]. The SWCNTs were manually applied by direct dry transfer from the nitrocellulose filter onto the top surface of the DRW, as shown in Fig. S2. SWCNT layers with an 80% optical transparency and 5 mm length, while covering the whole rod width, were studied. The illumination inducing the phase shifting effect was carried out with a green laser source with a wavelength of 532 nm. The laser was connected to a DC power supply at 3.7 V and 0.34 A, corresponding to $\sim 37 \text{ mW}$ light power at room temperature. The incident optical power of the light source was determined with a “Sper Scientific 840011” laser power meter. Two-port S-parameter measurements were performed with a Rohde & Schwarz ZVA-24 Vector Network Analyzer with extension head modules in the 75–500 GHz frequency range. Static measurements were made in five waveguide bands (WR-10, WR-6, WR-5, WR-3, and WR-2) to cover the whole frequency range.

References

- [1] M. E. Itkis *et al.*, "Purity evaluation of as-prepared single-walled carbon nanotube soot by use of solution-phase near-IR spectroscopy," (in English), *Nano Letters*, vol. 3, no. 3, pp. 309-314, Mar 2003.
- [2] M. E. Itkis, D. E. Perea, R. Jung, S. Niyogi, and R. C. Haddon, "Comparison of analytical techniques for purity evaluation of single-walled carbon nanotubes," (in English), *Journal of the American Chemical Society*, vol. 127, no. 10, pp. 3439-3448, Mar 16 2005.
- [3] A. D. McNaught, A. Wilkinson, and International Union of Pure and Applied Chemistry., *Compendium of chemical terminology : IUPAC recommendations*, 2nd ed. Oxford England ; Malden, MA, USA: Blackwell Science, 1997, pp. vii, 450 p.
- [4] I. V. Anoshkin, A. G. Nasibulin, P. R. Mudimela, J. Raula, V. Ermolou, and E. I. Kauppinen, "Selective chemical functionalization of carbon nanobuds," (in English), *Carbon*, vol. 50, no. 11, pp. 4171-4174, Sep 2012.
- [5] J. M. Dai, J. Q. Zhang, W. L. Zhang, and D. Grischkowsky, "Terahertz time-domain spectroscopy characterization of the far-infrared absorption and index of refraction of high-resistivity, float-zone silicon," (in English), *Journal of the Optical Society of America B-Optical Physics*, vol. 21, no. 7, pp. 1379-1386, Jul 2004.
- [6] D. V. Lioubtchenko, S. N. Dudorov, and A. V. Raisanen, "Development of Rectangular Open Dielectric Waveguide Sections for the Frequency Range of 75-110 GHz," in *2001 31st European Microwave Conference*, 2001, pp. 1-4.