Supporting Information

Holey Single-Walled Carbon Nanotubes for Ultra-Fast Broadband Bolometers

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Bolometer performance

Bolometers' operation is usually based on the change of a registered signal under the IR radiation due to the heating of the sensing material. The well-known expression for bolometer's voltage sensitivity is:¹

$$R_{v} = \frac{IR\alpha\varepsilon}{G_{th}\sqrt{\left(1+\omega^{2}\tau^{2}\right)}},$$
(S1)

where G_{th} is the thermal conductivity from the sensor to the substrate, ε is the coefficient of IR radiation absorption, R is the sensor resistance, α is the temperature coefficient of resistance (TCR) given by $\alpha = \frac{1dR}{RdT}$, I is the current through the sensor, ω is the radiation modulation frequency and τ is the bolometer response time, which characterizes the operation speed:¹

where C is the thermal capacitance of the sensor.

Characteristics of bolometer prototypes measured at $\lambda = 1560$ nm

Table S1. Characteristics of bolometer prototypes fabricated using pristine and holey SWCNT

Oxygen plasma	Voltage sensitivity,	Response time,	NEP
treatment time [s]	Rv [V/W]	τ [ms]	[10 ⁻⁹ W Hz ^{-1/2}]
0	3.50±0.20	1.6±0.1	3.7±0.8
10	1.20±0.05	2.2±0.2	25±7
30	2.64±0.10	3.2±0.2	23±7
40	4.00±0.30	3.1±0.2	8.3±2

films, measured at $U_{bias} = 1$ V and the laser wavelength of $\lambda = 1560$ nm at T = 300 K.

According to Expression S1 the only parameter which determines wavelength dependence of voltage sensitivity is the absorption coefficient. Other parameters (like TCR, resistance and thermal conductivity) do not depend on the wavelength. Sensitivities measured for the sample made of pristine SWNTs at 650 and 1560 nm are 4.73 and 3.55 V/W (Table 1 and Table S1), which are respectively proportional to the absorption coefficients of 37.1% and 29.6% at the corresponding wavelengths (Figure S2 c) within the measurement accuracy. Thus, we can extrapolate the response values measured at one wavelength to the whole range using the absorption spectra.

Heterogeneous model of conductivity of SWCNT films treated with plasma

Resistance temperature dependence of SWCNT films might be well described by the heterogeneous model.^{2,3} According to this model the resistance of a material might be determined by well-conducting regions connected by nonconducting parts and defined by two

terms. The first one is associated with fluctuation assisted tunneling (FAT) between conducting regions and give the main contribution to resistance at low temperature limit where the thermal voltage fluctuation is not high. The second one is determined by the intrinsic conductivity of SWCNTs in the film. Here backscattered phonons give the main contribution to the resistance at high temperatures.

We apply the heterogeneous model to pristine and plasma treated SWCNT films using the same procedure as described in ref. 3. The measured sheet resistance is normalized to the sheet resistance value at 300 K for all samples prior to fitting. The normalized sheet resistance dependence is approximated by the sum of two functions using least-square procedure:

$$R_{\Box}(T)/R_{\Box}(300K) = F_1(T) + F_2(T).$$
(S3)

The first function is the contribution of the SWCNT conductivity:

$$F_1(T) = A_m exp\left(-\frac{T_m}{T}\right)$$
(S4)

and the second one is associated with tunneling between conducting regions (FAT contribution):

$$F_2(T) = A_t exp\left(-\frac{T_t}{T+T_s}\right).$$
(S5)



Figure S1. Approximation of the sheet resistance dependence on temperature with the heterogeneous model. (a) Dependence of the normalized sheet resistance of pristine SWCNT films on temperature and fitting of two contributions: FAT and SWCNT part. (b) Dependence of the normalized sheet resistance of pristine and oxygen plasma treated films on temperature and results of fitting of the heterogeneous model.

We determine A_m , T_m , A_b , T_t and T_s parameters of the model by approximation (Table S1). The adjusted R^2 values in the fitting procedure are also given in the table. The adjusted R^2 is the parameter, which quantify how well a model fits the experimental data; the closer one is to the 1 the better the fit. For the pristine film both contributions are distinguished (Figure S1a) and the derived parameters are consistent with the values for the pristine films in ref. 3. In the case of the treated films the intrinsic part of the CNTs resistance can be neglected and the resistance dependence is described by term (S5) in the whole considered temperature range (Figure S1b).

 Table S2. The fitting parameters of heterogeneous model for pristine and plasma treated

 SWCNT films.

Sample	FAT contribution	SWCNT contribution

	A_t	T_t	T_s	$Adj. R^2$	A_m	T_m	$Adj. R^2$
pristine	0.69	25.22	6.99	0.99999	5.71	934.1	0.99969
treated 10 s	0.72	118.0	60.5	0.99975	-	-	-
treated 25 s	0.20	732.0	163.8	0.99978	-	-	-
treated 50 s	0.15	773.8	109.9	0.99893	-	-	-
treated 75 s	0.15	704.9	69.53	0.99925	-	-	-
	1						

Characterization of the material



Figure S2. Optical spectra of pristine and holey SWCNTs. (a) Transmittance, (b) reflection and (c) absorption of free-standing pristine SWCNTs and tubes treated in oxygen plasma at different exposure time. All films are densified with ethanol.

The peaks around 4100, 7650 and 11000 cm⁻¹ correspond to the electronic transitions between Van Hove singularities in semiconducting (S_{11} and S_{22}) and metallic (M_{11}) tubes, correspondingly. Two lines at 1160 and 1560 cm⁻¹ can be assigned to C=C and C-O stretching vibrations.⁴ The transitions due to the van Hove singularities in the electronic spectrum almost disappear in the treated SWCNTs as their structure is damaged. Some part of the material is oxidized so the films become more transparent and less reflecting at high degree of the treatment. The last fact can be explained by poor conductivity of treated films comparing to pristine ones.

Scanning electron microscopy images (Figure S3) reveal networks of randomly oriented pristine and plasma treated SWCNTs with the similar morphology. Though, the catalyst particles are better recognized in the plasma treated film.



Figure S3. SEM images of (a) pristine SWCNT film placed onto quartz substrate, (b) the same film treated with oxygen plasma with the treatment time of 100 s.

We evaluate films' chemical composition by XPS. The acquired XPS survey spectra reveal C, O, Fe, N and Si which are represented by corresponding photoelectron peaks and Auger lines in a good agreement with the literature reference (Figure S4). Peaks related to Si 1s and Si 1p are due to signals from the substrate.

XPS data yield that C1s peak, O1s peak change significantly after application of oxygen plasma. We observe an increase of intensity of O1s peak and O KLL line while C1s peak is reduced.



Figure S4. XPS spectra of pristine and oxygen plasma treated SWCNT films (50 s, 100 s at 100 W) placed over Si/SiO₂ substrate.

C1s core level spectra of the studied films are presented in Figure S5. XPS spectrum of the pristine SWCNT film is characterized mainly by *sp*²-hybridized carbon (284.5 eV) ^{5,6} with a minor presence of Fe-C bond at 283.6 eV which should originate from Fe₃C compound. A hump at $E_b = 286.5-287$ eV might be attributed to epoxy and hydroxyl groups.^{6–10} The p-plasmon is at 289.9 eV, at this energy we might also expect the peak to be related to C=O bond or O-C=O bonds (in case of the treated samples).

Deconvolution of the C1s spectrum of the treated films suggest a consecutive increase of C-O peak and the shoulder at 289.9 eV with the exposure time while the intensity of sp^2 -peak is reduced. The treatment facilitates sp^3 -hybridized carbon peak appeared at 285.6 eV.



Figure S5. XPS core level C1s spectra of pristine and oxygen plasma treated SWCNT films on Si/SiO₂ substrate.

Deconvolution of the O1s spectrum of the pristine tubes might hint on the peaks associated with C-O-H ($E_b = 533.0 \text{ eV}$) corresponding chemically bonded oxygen and C=O bonds ($E_b = 531.9 \text{ eV}$) referring to the adsorbed oxygen (Figure S6). We also might identify humps due to Me-O bond at (530.6 eV). Oxygen plasma action yields an increase in C-O-H and C=O as well as Me-O peak intensities. There can be O-C=O related and hydroxide-related peaks found in the treated films.

Plasma treatment increases the oxygen content toward attainment of approx. 32.0 at.% for 50 s of the treatment and ca. 34.7 at.% for 100 s of the treatment at 100 W when compared to 2.6 at.% for the pristine tubes (the detailed comparison is given in the Table S2).

Spectra related to Fe2p are presented in the Figure S7. Fe2p peak corroborates presence of metallic Fe (706.8-706.9 eV), F-C (707.4-707.9 eV) and Fe oxide (709.6-714.0 eV) appeared from catalytic particles which inherently present in SWCNT films. Fe-C peak might stem from Fe₃C compound. It is worth noting that even pristine tubes appear to contain oxidized Fe. We fit several Fe oxide-related peaks which are shown to be due to α - or γ - Fe oxides.¹¹ The intensities

of Fe oxide peaks are facilitated by plasma treatment. The amount of metallic Fe is reduced after the treatment, depending on the treatment duration.

We calculated the atomic ratio of the elements based on the relative intensity of the Fe $2p_{3/2}$, C 1s and O 1s peaks and the ratio of the chemical bonds using results of spectra deconvolution. The results are presented in the Table S2 and S3.



Figure S6. Deconvolution XPS core level O1s spectra of pristine and oxygen plasma treated SWCNT films on Si/SiO₂ substrate. Red line envelopes curves of all fitted peaks.



Figure S7. Deconvolution XPS core level Fe2p spectra of pristine and oxygen plasma treated SWCNT films on Si/SiO₂ substrate. Red line envelopes curves of all fitted peaks.

 Table S3. Relative atomic concentrations of elements in pristine and oxygen plasma treated

 SWCNT films.

Sample	C1s, at.%	N1s, at.%	O1s, at.%	Si2p, at.%	Fe2p3, at.%
100s	58.15	1.65	34.74	4.78	0.68
50s	66.16	0.10	32.04	0.83	0.87
Pristine	94.77	1.54	2.61	0.66	0.42

Table S4. Ratio of the chemical bonds (C1s, O1s and Fe2p) based on results of spectra deconvolution.

Carbon chemical bonds, %				
Treatment time, s	100	50	Pristine	
Fe-C	1.5	2.5	0.7	
C=C	32.5	38.4	94.4	
C-C	2.7	2.6	0.0	
C-0	20.6	17.1	1.8	
С=О	4.7	6.1	0.0	
Oxygen chemical bonds, %				

Trea time	atment e, s	100	50	Pristine
Me-	-0	1.8	2.0	0.4
C=0	0	9.8	9.4	0.9
C-C)-Н	23.0	19.6	1.3
0-0	C=O	2.6	1.4	0.0

Iron chemical bonds, %

Treatment time, s	100	50	Pristine
Fe-met	0.04	0.04	0.10

Fe-C	0.02	0.02	0.15
Fe2O3-p1	0.21	0.15	0.11
Fe2O3-p2	0.35	0.67	0.05
Fe2O3-p3	0.10	0.00	0.00

Iron oxide phases, %

Treatment time, s	100	50	Pristine
α-Fe2O3	0.36	0.45	0.11
γ-Fe2O3	0.30	0.37	0.06

We made FETs of SWCNT film on oxidized silicon substrate to verify the role of different oxidation mechanisms which might take place during the oxygen plasma treatment. The results of stepwise treatment of one FET are presented in Figure S8. The distance between the source and the drain is 40 μ m. The drain current variation with gate voltage change in the range -20 V to 20 V is in the order of 10-15% and does not depend on the treatment time.



Figure S8. Transfer ($I_D - V_{GS}$) characteristics at $V_{SD} = 0.5$ V of FETs made of SWCNT film, different time of oxygen plasma treatment: (a) pristine film, (b) 200 s, (c) 800 s.

References

1. A. Rogalski, Infrared Detectors, CRC Press, Boca Raton, USA, 2011.

- 2. A. Kaiser, Rep. Prog. Phys. 2001, 64, 1.
- V. I. Tsebro, A. A. Tonkikh, D. V. Rybkovskiy, E. A. Obraztsova, E. I. Kauppinen, E. D. Obraztsova, *Phys. Rev. B*, 2016, 94, 245438.
- 4. L. Hussein, RSC Adv, 2016, 6, 13088.
- 5. T. I. T. Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin, N. M. D. Brown, *Carbon*, 2005, **43**, 153.
- P. P. Pal, T. Larionova, I. V. Anoshkin, H. Jiang, M. Nisula, A. A. Goryunkov, O. V. Tolochko, M. Karppinen, E. I. Kauppinen, A. G. Nasibulin, *J. Phys. Chem. C*, 2015, 119, 27821.
- 7. P. C. Ma, J. Kim, B. Z. Tang, Carbon, 2006, 44, 3232.
- 8. S. Pei, J. Zhao, J. Du, W. Ren, H. Cheng, Carbon, 2010, 48, 4466.
- S. Kim, S. Zhou, Y. Hu, M. Acik, Y. J. Chabal, C. Berger, W. de Heer, A. Bongiorno, E. Riedo, *Nature Mat.*, 2012, 11, 544.
- Y. Yamada, H. Yasuda, K. Murota, M. Nakamura, T. Sodesawa, S. Sato, *J. Mater. Sci.*, 2013, 48, 8171.
- A. P. Grosvenor, B. A. Kobe, M. C. Biesinger, N. S. McIntyre, *Surf. Interface Anal.*, 2004, 36, 1564.