Strong and Reversible Modulation of Carbon Nanotube-Silicon Heterojunction Solar Cells by an Interfacial Oxide Layer

Yi Jia[1,2], Anyuan Cao[3*], Feiyu Kang[1], Peixu Li[2], Xuchun Gui[4], Luhui Zhang[3], Enzheng Shi[3], Jinquan Wei[2], Kunlin Wang[2], Hongwei Zhu[2], Dehai Wu[2*]

[1] Graduate School at Shenzhen, Tsinghua University, Shenzhen, Guangdong Province, 518055, P. R. China

[2] Key Laboratory for Advanced Materials Processing Technology and Department of Mechanical Engineering, Tsinghua University, Beijing 100084, P. R. China

[3] Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China

[4] State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China

Supplementary Information:

Table S1. Characteristics of the CNT-Si solar cell (in Fig. 2a) at different air storage times under AM 1.5G, 100 mW/cm^2 illumination.

Time **(h)**	***Oxide-thickness*** **(Å)**	V_{oc} **(V)**	J_{sc} **(mA/cm^2)**	***FF*** **(%)**	J_0 **(μA/cm^2)**	***n***	R_s **(Ω)**	R_{sh} **(MΩ)**	***η*** **(%)**
0	0	0.18	11.4	23.1	93.9	3.3	40.0	0.012	0.5
8	--	0.31	22.8	32.7	13.5	2.8	35.9	0.176	2.3
26	4.6	0.38	25.1	41.9	9.0	2.9	35.5	0.730	4.0
49	5.8	0.46	24.1	55.8	4.37×10^{-2}	2.3	34.9	1.282	6.3
97	6.4	0.50	24.7	61.9	2.22×10^{-2}	1.5	32.6	1.852	7.7
140	8.7	0.54	24.3	66.9	5.0×10^{-3}	1.4	34.4	3.030	8.8
native oxide	20~30	0.53	17.6	15.6	--	--	--	--	1.44

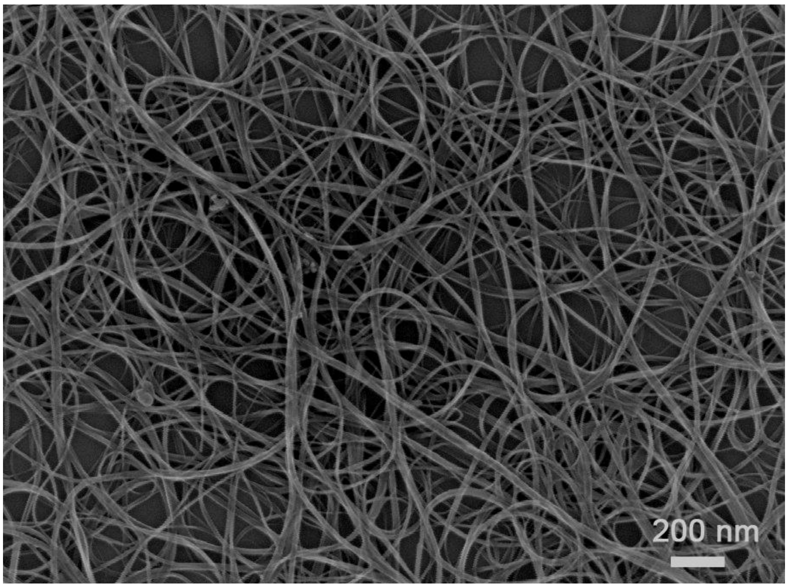

Figure S1. SEM image of the CNT film used for making CNT-Si solar cells.

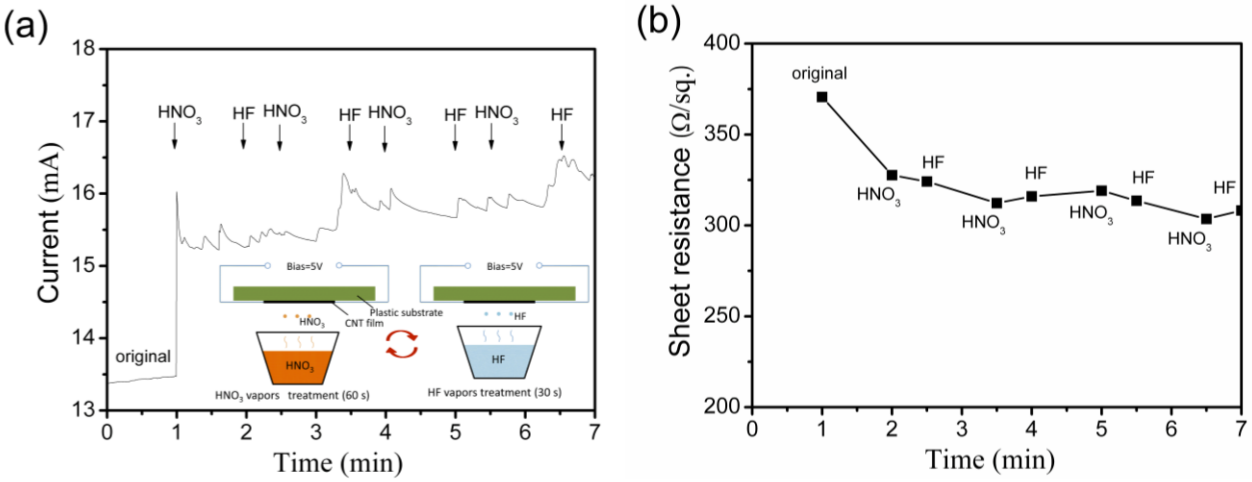

Figure S2. Conductivity of CNT film during HNO_3 and HF vapors treatments. (a) Real time recording of the current through the CNT film during HNO_3 and HF vapors treatments. Inset, schematic of the treatment process, the CNT film was fixed on a plastic substrate and applied by a constant bias voltage of 5 V. (b) Change in the CNT sheet resistance of solar cells during HNO_3 and HF vapors treatments.

Experimental Section

Synthesis of CNT films. CNT films were synthesized by a floating catalyst chemical vapor deposition process in a horizontal furnace, with xylene as carbon source, ferrocene (0.36 mol/L) and sulfur (0.036 mol/L) as catalyst precursor. The feeding rate (2~4 μL/min) was accurately controlled by an automatic syringe pump. After introduced into quartz tube, the mixture was vaporized and carried to reaction zone by a gas mixture of Ar (2500 sccm) and H_2 (600 sccm). Reaction zone temperature was 1150~1170 °C. As-prepared CNT films were collected by a nickel foil placed at the end of quartz tube. The CNT film was directly picked up in freestanding structure from the nickel foil and immersed into H_2O_2 (30 wt.%) and HCl (36.5 wt.%) to remove amorphous carbon as well as catalyst residue, then rinsed by distilled water. The purified CNT film floating on distilled water can be fully expanded into a thin uniform film with addition of several drops of ethanol on the water surface. The optical transmittance and sheet resistance of CNT films are characterized to be >85 % and <200 Ω/sq., respectively.

Fabrication processes. The CNT film floating on water was transferred onto an n-type Si/SiO_2 substrate (resistivity 2~4 Ω cm) with 0.09 cm^2 active Si windows pre-etched. Ti/Au electrode was pre-deposited on the back side of the silicon substrate to form ohmic contact to Si. Silver wires were connected to the front (CNT film) and back (Ti/Au) electrodes using silver paint, respectively. The current density was calculated using the active window area (0.09 cm^2) for each cell. Because a thin natural oxidation layer would grow during the cell fabrication processes, to obtain a fresh CNT-Si interface without native oxide, a droplet of 2 wt.% HF was added onto the CNT film for 10 seconds after cell assembly. As the CNT films have a porous structure, HF can easily penetrate the film and access the Si surface underneath to etch the natural oxidation layer in the active area. Then we washed the cell with deionized water and dried by nitrogen gas. After that, we immediately tested the cell under solar simulator (Newport 91195 class A) and Keithley 2601, as the 0 h curve in Fig. 2a. The solar cell was kept at a temperature humidity chamber with a temperature of 25 ℃ and humidity <5 % to gradually grow oxide over a period of 251 hours and the cell performance was tested.

The 5 control samples in auger electron spectroscopy detection (Fig. 3a) were carefully made from the same raw materials (same piece of CNT film and silicon wafer) and identical fabrication process as the tested cell in Fig. 2a, followed by being kept under the same temperature (25 °C) and humidity (<5%) in air for 0 h, 26 h, 49 h, 97 h and 140 h, respectively. The covering CNT films were removed from those control samples by ultrasonic cleaning and the underlying silicon substrates were used for Auger spectra analysis.

To study the effect of thicker oxide on CNT-Si solar cell performance, we used long time stored silicon substrates (more than one year) to configure solar cell, and the conventional process of 2 wt.% HF rinsing onto silicon substrate surface before cell fabrication was neglected. As a result, there was a thicker native silicon oxide layer (compared 251 hours stored substrate.). Based on this, we fabricated CNT-Si solar cell and tested its performance (Figure 2c).

To treat the CNT-Si solar cells with HF and HNO_3 vapors following the process in Figure 4, the cell was placed downward on the opening of small HF (40 wt.%) and HNO_3 (68 wt.%) vials and face the HF vapor for 15 seconds (to etch oxide) and HNO_3 vapor for 90 seconds (to grow oxide), respectively and in an alternative way. Each time after treatment by one acid vapor, the solar cell characteristics were tested and the procedure was repeated for 6 cycles.

Characterization of CNT-Si solar cells. The solar cell performances at different storage times were characterized by a solar simulator (Newport 91195 class A) with a light intensity of 100 mW/cm^2, which was calibrated by a standard Si module (Newport, 91150V). The current density-voltage (J-V) characteristics were measured by Keithley 2601. The Si substrates were measured by Auger electron spectroscopy (PHI-700, ULVAC-PHI) with the depth sputtering rate of 1 nm/min for standard SiO_2 sample. The log(J)-V curves of the CNT-oxide-Si solar cell were tested from 50 K to 300 K by Physics Performance Test System (PPMS-9T). The shunt resistances (R_{sh}) and series resistances (R_s) of dark I-V curves at different storage times as listed in Table 1 were calculated as the reciprocals of slopes in reverse bias region and high (0.5~1 V) forward bias region, respectively. The saturation current densities (J_0) in Table 1 were obtained by fitting the experimental data to Shockley Equation:

$$J=J_0\{\exp[q(V-IR_s)/nkT]-1\}$$

Where J is current density in dark curve, q is the electron charge, V is the voltage and R_s is the series resistance.