A complete scheme for creating predefined networks of individual carbon nanotubes

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Supplementary Information

Pillar Fabrication:

Silicon pillars were fabricated from p-type silicon (450 µm thick), with a 500 nm thick thermal oxide layer. Photo-lithography was used to define the array of pillars and Reactive Ion Etch, followed by Deep Reactive Ion Etch were used to etch away the oxide and silicon (respectively), to create high aspect ratio pillars. The height of the pillars was 20 µm, and the pitch ranged from 5 to 20 µm, with the pillars arranged in large square grids. Other array assemblies were designed as well with other forms of pillars, with round pillars found to be the best choice for creating suspended networks of CNTs. The key factor in the growth of the suspended CNTs is that they self-assemble into well defined networks, as defined by the geometry of the pillar network. All masks and samples were fabricated in the electrical engineering microfabrication facility at Tel-Aviv University.

CVD Growth:

CVD growth of the CNTs was implemented in a standard setup consisting of a 1" quartz tube furnace (LindbergBlueM Minimite 1100 tube furnace), gas flow controllers, and an in-house designed computerized control system. The protocol for growing the CNTs used here was as follows: Catalysts for the CVD production of CNTs were coated on the silicon dioxide pillar tops by placing a suspension of nanoparticle catalysts (suspensions of iron salts ($Fe(NO_3)_3$) (Sigma-Aldrich) in iso-propanol (IPA)) upon an O_2 plasma-cleaned poly-dimethyl siloxane (PDMS) film, which was then stamped onto the pillar tops.

Samples were placed within the tube furnace, which was then purged by flowing hydrogen gas at 1000 sccm, for 10 min. The furnace was then heated to 860 °C, in the presence of hydrogen, at which point ethylene gas, at 20 sccm, was added for 9 min. After the growth period, the furnace was allowed to cool down to room temperature, accompanied by a constant flow of hydrogen gas only (at a rate of 500 sccm).

Imaging and Spectroscopic Equipment:

After the CVD growth, the growth results were verified using a high-resolution scanning electron microscope (JEOL JSM-6700 FEG) operating at 1kV.

TEM analysis of the stamped nanotubes, as described in the text, was done by stamping the CNTs directly onto a TEM viewing grid which consisted of a silicon substrate, covered by a 200 nm thick, LPCVD silicon nitride layer (DuraSiN meshes, Protochips Inc.). The center of the grid contains a large square hole, 0.5 cm^2, over which only a thin nitride layer exists. In this thin film of nitride are circular holes, 4 µm in diameter, through which the electron beam in the TEM can pass uninhibited, allowing maximal contrast, whereas the 200 nm thick nitride film remains opaque. The TEM used was a high-resolution TEM (Philips Tecnai F20), operating at 200 kV.

Raman mapping equipment entailed an in-house designed RS system, consisting of Andor Shamrock 303i spectrograph combined with Andor Newton/iDus cooled CCD camera, 532 nm laser (B&W Tek), and a self-made confocal optical microscope with a computerized control system, which allows the user to move the sample and analyze the obtained spectrum simultaneously, thus scanning and raster-mapping the desired area. Pixelization was determined by the piezo-motor setup driving the sample holder (minimal step 0.1 µm), as well as the spot-size of the input laser, at ~0.5 µm. Each pixel in the map consists of the integral within a "spectral windows" around the relevant Raman peak.

Stamping Method:

Stamping the suspended CNTs from the pillar tops to target surfaces entailed placing the pillared substrate with the suspended CNTs face down and above a target surface, and applying manual pressure. In addition, it was found that adding a liquid between the two surfaces prior to contact was essential for transfer (as explained in the text). De-ionized water was found to provide the best results for this requirement. Ethanol and hexane provided similar, but somewhat inferior, results. Target substrates included silicon, silicon dioxide, and gold on silicon dioxide.

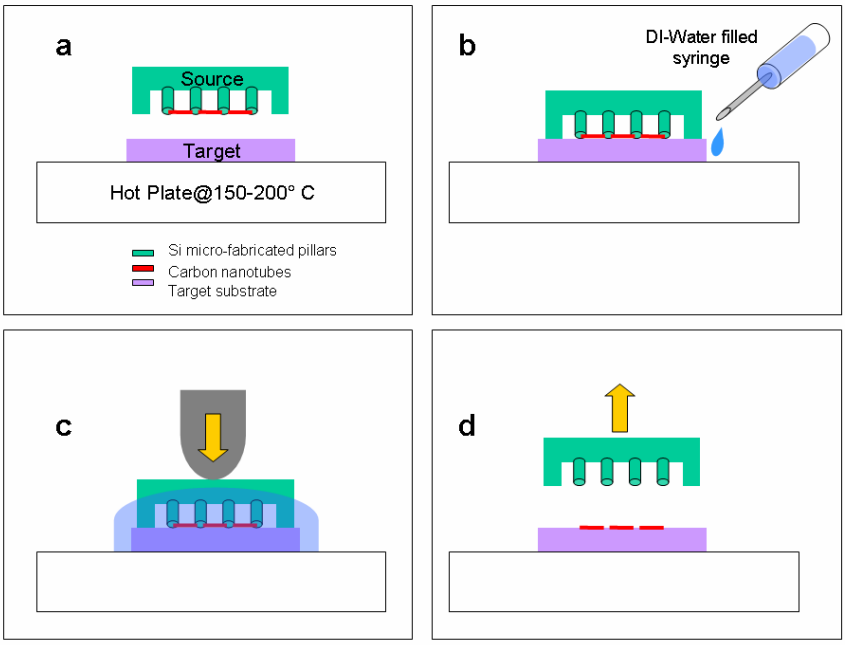

Figure s1. Schematic of the stamping method: The stamping was done directly on a standard hot plate heated to 150-200 °C. (a) The target substrate is placed on the hot plate for a few minutes (to reach equilibrium) and then the source substrate (the stamp with the pillars and the nanotubes) is placed on top of the target manually, using a tweezers. (b) The source is held down onto the target using a tweezers and then a few drops of DI-water are deposited near the target/source using a syringe. The droplets are dispensed on or near the (heated) target substrate, which is typically larger than the source substrate. Furthermore, the droplets are placed as near as possible to the sandwiched region between the two substrates, to allow the heated water to enter the spacing between the substrates. (c) The water droplets coalesce around the target/source interface and then quickly evaporate. The source substrate is pushed down against the target. (d) After the water has completely dissipated, the source substrate is removed, leaving the suspended nanotubes on the target.

Electrical measurements:
CNT FETs were realized by stamping CNT onto oxidized p-type silicon wafers (500 nm thick oxide). Electronic measurements were carried out by measuring the source-drain current of the CNT transistor, while sweeping the gate-source voltage and keeping the drain-source voltage constant. V_{DS} was 0.1 V. The gate-source leakage current was validated to be negligible in all instances. All measurements were implemented in an enclosed probe station (Karl-Suss PM5), in conjunction with a pico-ampermeter (Hewlett Packard 4140B). Data was then analyzed using Igor Pro software.

Supplementary Results

Suspended CNT Growth:
Figure s2 displays HRSEM images of several, high yield, suspended networks of nanotubes bridging micro-fabricated pillars. The size and pitch of the pillars correlates with the yield of suspended nanotube growth. Small pillars of 2-5 μm diameter with spacing of 10-15 μm proved nearly 100% yields of suspended nanotube growth between neighboring pillars. Larger diameter pillars, or ones with a smaller pitch will results in more than one nanotube suspended between neighboring pillars, as well as a larger probability of undesirable diagonal growth. Furthermore, large spacing prevents nanotubes from reaching neighboring pillars resulting in lower yields.

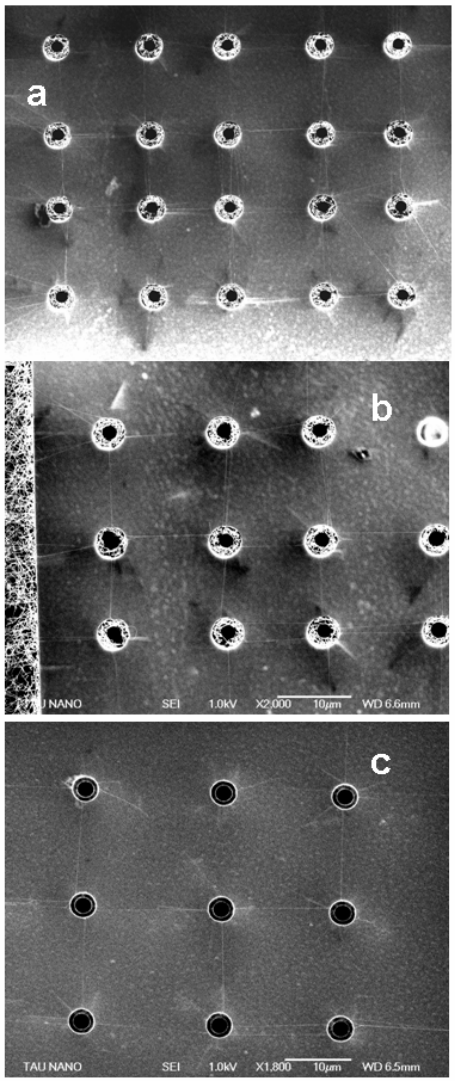

Figure s2. Images of suspended nanotubes prior to stamping. Suspended nanotube yield reaches 100% for some arrangements. The black holes in the center of the pillars results from the DRIE etching.

Stamping Results:

Figure s3 displays results of nanotube transfer. The predominantly horizontal arrangement of stamped nanotubes (Figure s3a and s3b) is a testament of the flow within the tube furnace during the CVD growth, which is sometimes strong enough to partially align the nanotubes in the direction of the flow.

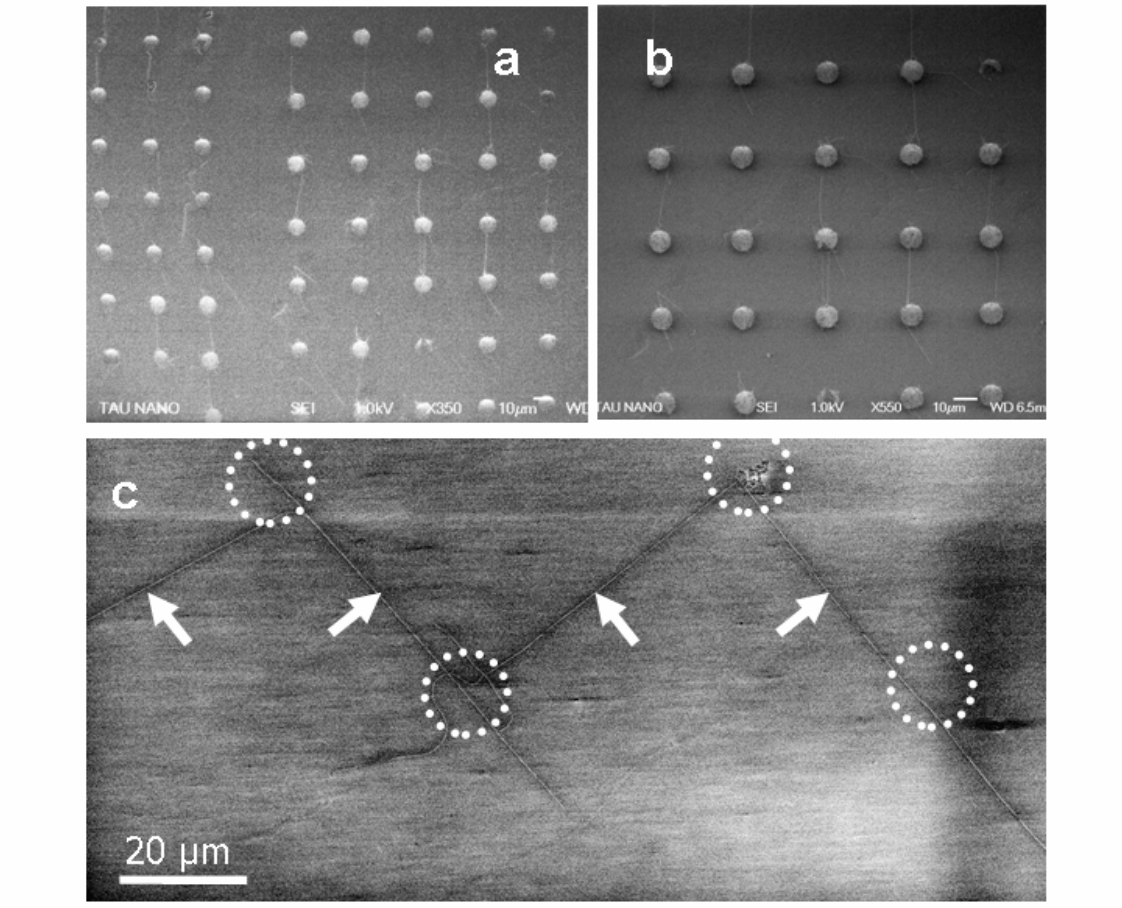

Figure s3. Stamping images. (a, b) Large arrays of transferred nanotubes, predominantly in the horizontal direction (corresponding with the direction of the gas flow). Spacing between the horizontal strains remains a near-constant 25 μm. (c) A sharp-angled set of transferred nanotube.