

# Supporting Information

## Spatially Selective, High Density Placement of Polyfluorene-Sorted Semiconducting Carbon Nanotubes from Organic Solvents

*Bharat Kumar,\*† Abram L. Falk,† Ali Afzali,† George S. Tulevski,† Satoshi Oida,† Shu-Jen Han,† James B. Hannon†*

† IBM T. J. Watson Research Center, 1101 Kitchawan Road, Yorktown Heights, NY 10598

## **Wafer fabrication**

Substrates for the carbon-nanotube chips were fabricated at IBM's Material Research Laboratory in Yorktown Heights, NY. Alignment marks were etched into eight-inch *n*-type silicon wafers with  $\text{C}_2\text{H}_4$  reactive ion etching. 10 nm of  $\text{HfO}_2$  dielectric was then deposited on the wafers, using atomic layer deposition. Trench arrays made out of either poly-silicon or  $\text{SiO}_x$  were then fabricated on the wafers. For the poly-silicon trenches, 5 nm of poly-silicon was deposited on the wafers. The trench patterns were then written onto the wafers with electron-beam lithography and Hydrogen silsesquioxane (HSQ) resist, and subsequently transferred to the poly-silicon with  $\text{HBr}$  and  $\text{Cl}_2$  reactive ion etching. The HSQ was then stripped off with diluted hydrofluoric acid. For the trench patterns made out of  $\text{SiO}_x$ , the HSQ trench pattern was patterned directly on the  $\text{HfO}_2$  dielectric. Once annealed, the HSQ resist functions as  $\text{SiO}_x$ .

Each chip is designed to each have 6144 carbon-nanotube transistors fabricated on it, with a pitch of 100 nm between devices. In the region where each device is to be fabricated, a trench array consisting of 20-30 trenches was fabricated. Each trench in this array has a width of 50-100 nm and a length of 750 - 1500 nm. The pitch of the trenches in these arrays was either 100 nm or 200 nm.

## **Device fabrication**

For most of our measurements, only the nanotube (or possibly multiple nanotubes) in a single trench is (are) contacted. To etch away the other nanotubes in the trench array, we used a PMMA / HSQ mask and oxygen reactive ion etching. The trench that is contacted is the same one for every device/trench array (i.e. trenches that look "good" under the scanning electron microscope are not

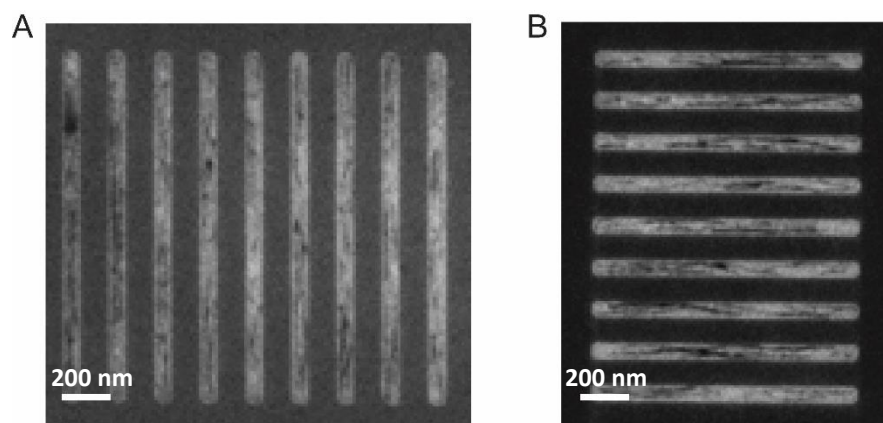
specifically selected). This procedure makes the conductance in each transistor derive from the nanotubes in a single trench. Occasionally, such as when taking the data in Figs. S5, we masked off several trenches at once and contacted the nanotubes in them in parallel.

For the chips with a poly-silicon trench pattern, the trench pattern is then wet-etched using  $\text{NH}_4\text{OH}$  heated to 50 °C. For the chips with  $\text{SiO}_x$  trench arrays, the  $\text{SiO}_x$  is just left on the chips, as it is resistive and does not interfere with our electrical characterization.

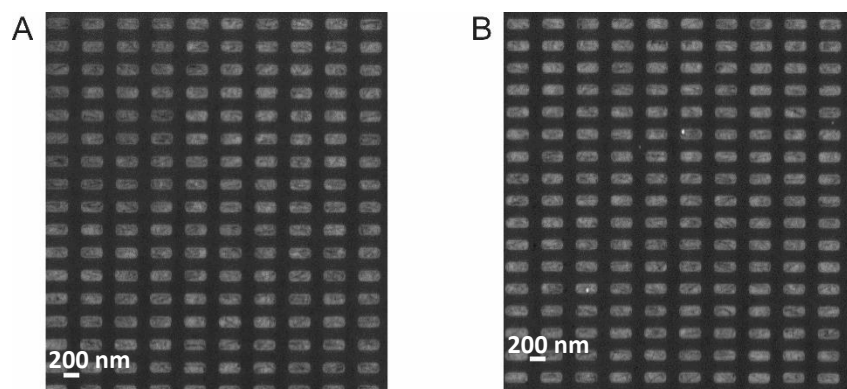
The chips are then annealed at 400 - 500 °C for 30 minutes in a vacuum oven. This annealing burns off the polymer coating on the nanotubes, as well as other organic contaminants on the chip based on comparing its electrical properties with that of the bare CNTs. To define contacts to the nanotubes, electron-beam lithography and conventional Ti/Pd evaporation is used.

#### **Electrical characterization: procedure**

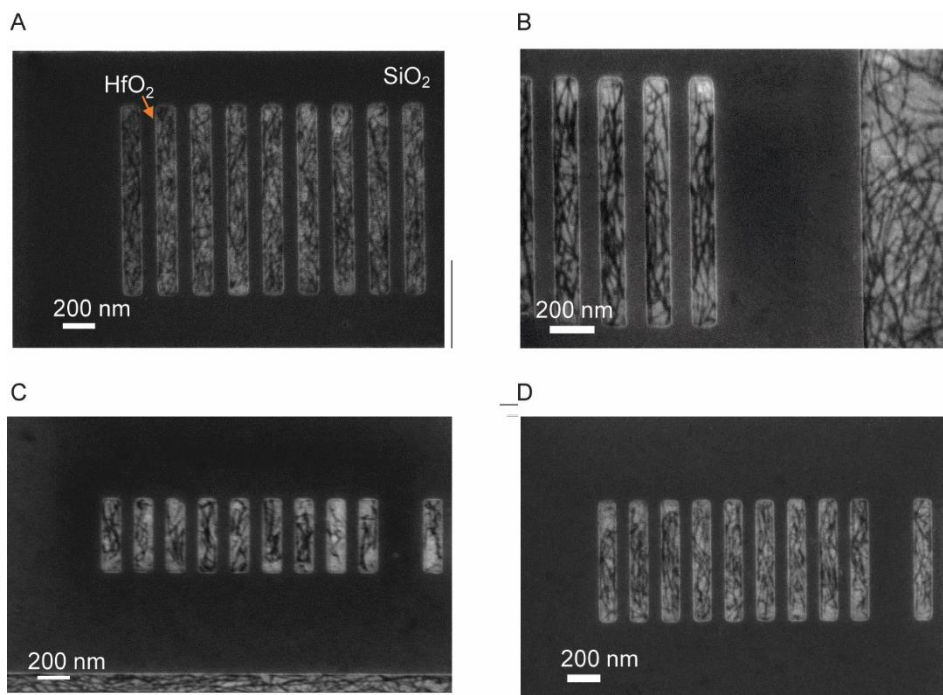
To characterize the nanotube transistors, we used a 25-probe Cascade summit semi-automated probe station in air. We fixed the source-drain bias at  $V_{\text{dd}} = 0.5 \text{ V}$ , and then, using the doped silicon substrate as a global back gate, swept the gate voltage ( $V_{\text{g}}$ ) from -3 V to +3 V. We generally characterized 24 x 16 blocks of transistors at once, a total of 368 devices per measurement block.



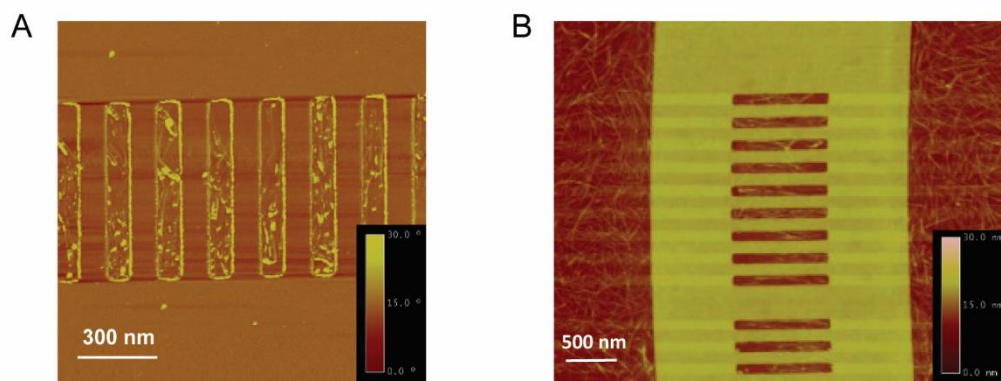
**Figure S1.** SEM images of different areas of substrate with 50 nm wide trenches (scale bar is 200 nm).



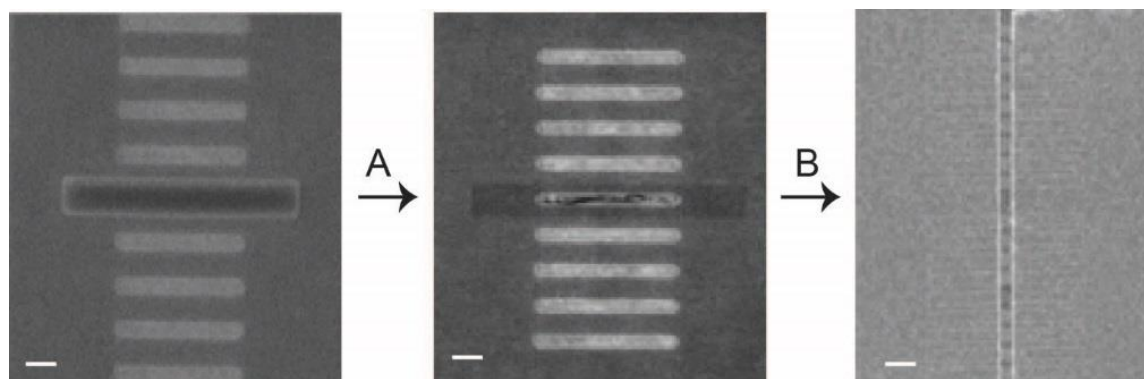
**Figure S2.** SEM images of placement in 100 nm wide trenches in large areas (scale bar is 200 nm).



**Figure S3.** SEM images of different areas of substrate with different lengths of 100 nm wide trenches.



**Figure S4.** AFM images of placed CNTs in 100 nm wide trenches.



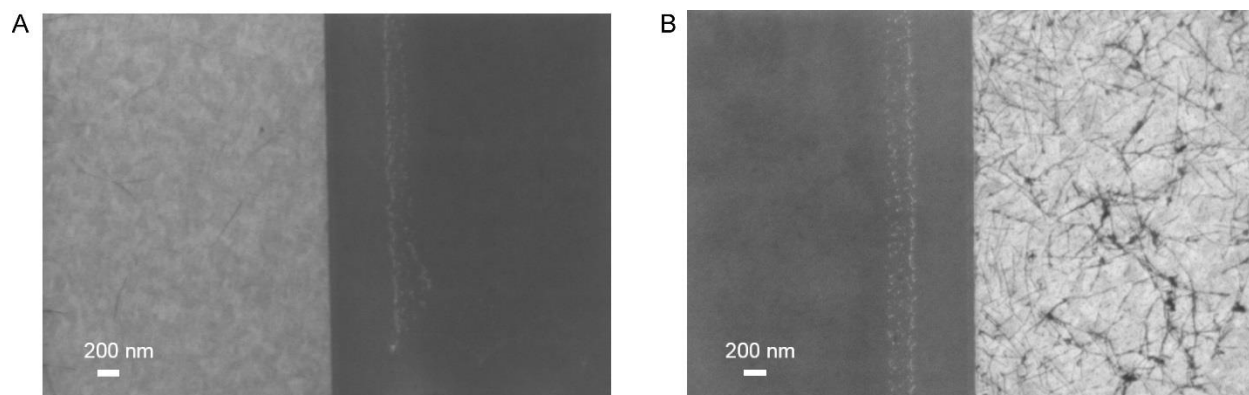
**Figure S5.** Fabrication steps for different trench devices, (A) masking of desired trench and (B) contact metal deposition (scale bar is 200 nm).

### **Mechanistic Studies:**

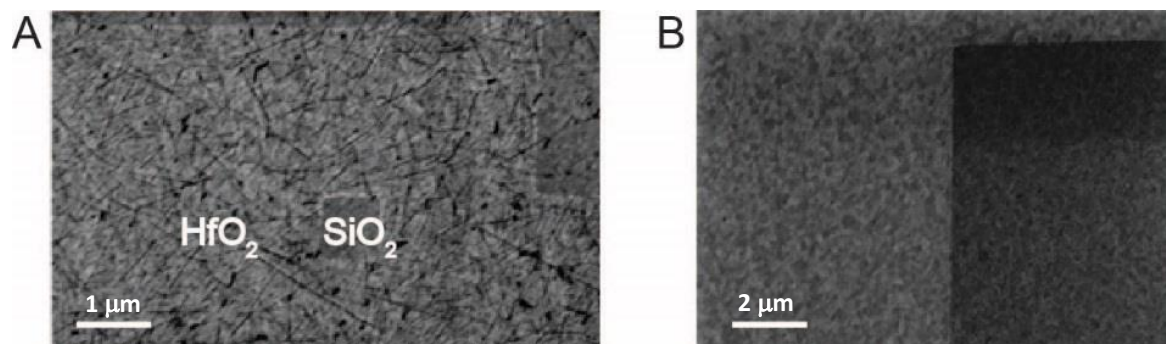
The sorted CNT-polymer solution was tested by addition of few drops of isolated diazonium salt solution of C<sub>5</sub> chain (figure S8). S<sub>22</sub> band at 1000 nm immediately starts disappearing after the addition of few drops of diazonium solution indicating that diazonium undergoing either charge-transfer or covalent bond formation with the tubes. We have also investigated any charge transfer interactions of aniline itself with the tubes. UV-Visible spectrum of the CNT-polymer solution in the presence of aniline over period showed no significant change (figure S9). This suggests that aniline itself does not undergo any charge-transfer interactions with the tubes or polymer.

XPS of monolayer was recorded before and after amyl nitrite treatment. The monolayer shows N1s peak at 403 eV. After brief amyl nitrite treatment, the intensity of this peak decreases and emergence of a new residual peak at 409 eV suggests surface reaction with amyl nitrite followed by decomposition of diazonium salt. XPS of drop casted isolated hexafluorophosphate salt of

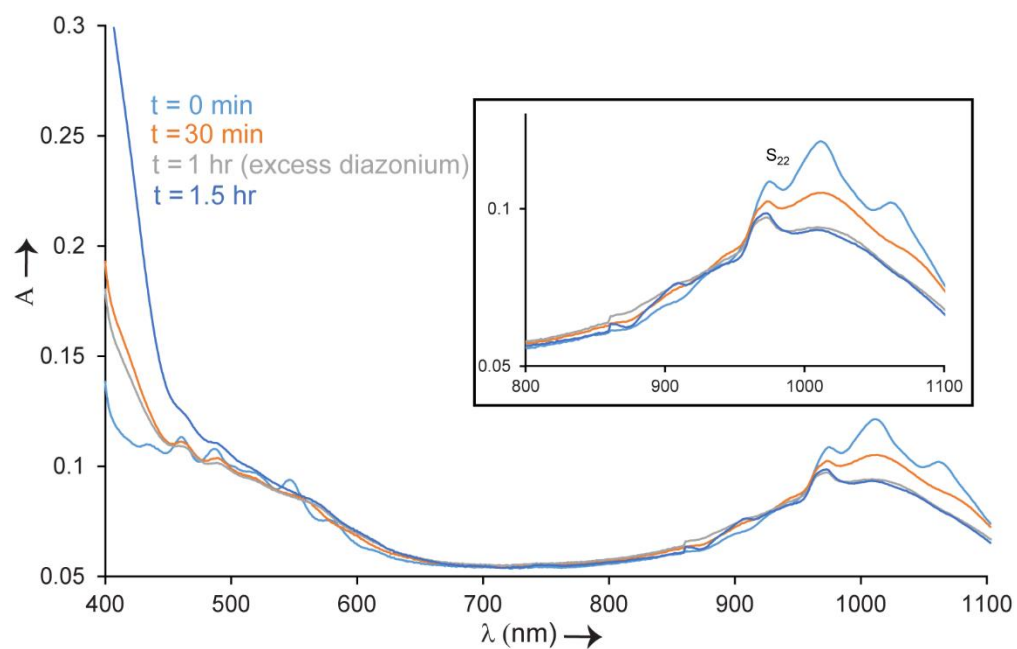
diazonium also showed similar two N1s peaks at 403 and 409 eV. The N1s peak at 409 eV is arising from decomposition of diazonium over time.



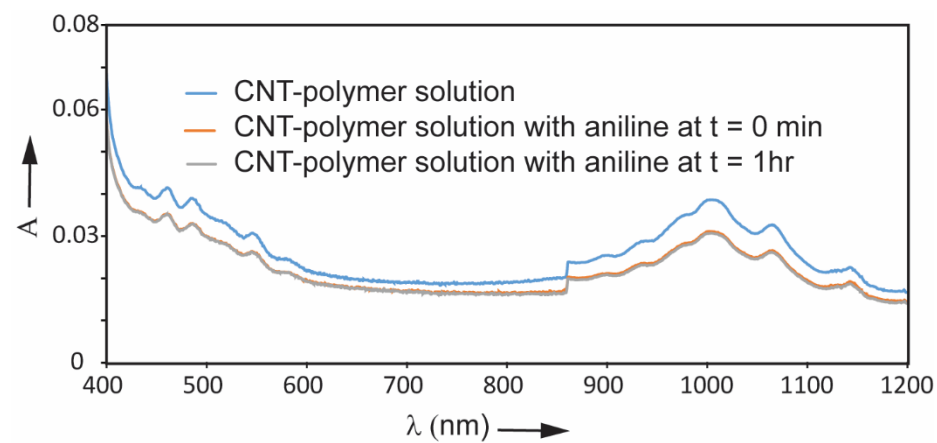
**Figure S6.** (A) SEM images of placed CNTs without diazotization and (B) SEM image of placed CNTs using amine monolayer using diazotized monolayer after 10 mins of sonication.



**Figure S7.** SEM images of placed CNTs (a) in the presence of monolayer and (b) in the absence of monolayer (scale bars 1  $\mu\text{m}$  for A and 2  $\mu\text{m}$  for B)



**Figure S8.** UV-visible spectrum of CNT-polymer solution after addition of 2 drops of 1 mM solution of diazonium salt with time (inset is zoom in view of changes in  $S_{22}$ )



**Figure S9.** Absorption spectra of CNT-polymer solution with only aniline at different times.