Supporting Information

Nanosoldering Carbon Nanotube Junctions by Local Chemical Vapor Deposition for Improved Device Performance

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1. Fabrication of Carbon Nanotube (CNT) Devices

CNT devices of two different geometries (network and crossbar) were prepared for our experiments. The carbon nanotube networks (CNN) were grown by chemical vapor deposition (CVD) using CH₄ gas as the carbon feedstock and H₂ as the carrier gas at 900 °C.¹ Ferritin (Sigma-Aldrich) catalyst was diluted in deionized water and spincast on thermally grown 90 nm and 300 nm SiO₂ films on highly doped silicon substrates, which were used as backgates. Prior to CNT growth, the catalyst was oxidized by heating the wafer to 900 °C, and cooled to room temperature in an air environment. The wafer was heated to 900 °C again with H₂ to reduce the catalyst, and CNTs were grown at 900 °C for 15 minutes under CH₄ and H₂ flows.

The CNTs for crossbar devices were grown by CVD using Ar and H₂, bubbled through chilled (0 °C) ethanol at 925 °C for 20 minutes.² For catalyst, a solution of ferritin diluted in deionized water was spincast onto a stable temperature (ST) cut quartz substrate to grow aligned CNTs. In order to achieve crossbar configuration, double transfer of CNTs was performed³ to thermally grown 200 nm SiO₂ films on highly doped silicon substrates, which were used as backgates. The transfer process involved depositing a thin carrier layer of Au and polyimide (PI) onto the CNTs, and peeling and transferring the carrier layer along with CNTs using an elastomeric stamp of polydimethylsiloxane (PDMS). After transferring CNTs to target substrates, the carrier layer was removed by oxygen reactive ion etching (RIE) and wet etching with a commercial solution (Au-TFA, Transene). This transfer process was repeated in orthogonal directions to achieve the crossbar configuration. Finally, the CNTs were patterned by standard photolithography and O₂ plasma etching. For electrodes, 40 nm to 80 nm of Pd was evaporated with a thin layer of Ti (0.5 nm) to improve the adhesion to the SiO₂ film, and patterned by lift-off. See Figure 1 in the main text for images of completed devices.

2. Device Preparation and Experimental Setup

After fabricating CNT devices, individual devices were wirebonded to the metal leads of a chip carrier using a 4524 Au Wire Ball Bonder (K&S). Figure S1a shows optical images of our wafer on a chip carrier with the inset image showing a zoomed-in view of CNT devices after wirebonding. Figure S1b shows a scanning electron microscope (SEM) image of one of our wirebonded CNT devices. SEM images were collected using Philips XL30 ESEM-FEG at an operating voltage of 1 kV.



Figure S1. (a) Optical images of carbon nanotube (CNT) devices on a chip carrier after wirebonding. **(b)** Scanning electron microscope (SEM) image of a wirebonded CNT device. Scale bar is 200 μm.

The precursor compounds, $Hf(BH_4)_4$ and $C_5H_5PdC_3H_5$ (CpPd(allyl)), were synthesized by methods described elsewhere.^{4,5} The gas delivery system to our home-built CVD chamber (see Figure 2b in the main text for a schematic diagram) consists of precursor reservoirs, two leak valves, and a stainless steel capillary doser. The flow was regulated by the leak valves and delivered to the sample through a stainless steel tube pointing directly at the CNT devices at a distance of about 2 cm. Prior to the CVD experiments, the precursors were kept in sealed stainless steel and glass containers under argon and stored in a refrigerator at -20 °C. For the actual experiments, the precursors were maintained at either 0 °C in an ice-water bath or at room temperature in order to achieve total pressure of ~10⁻⁴ Torr in the CVD chamber.

3. More Data Analysis and Control Experiments

All dc electrical characterizations in our experiments were performed with an HP 4155A semiconductor parameter analyzer. As noted in the main text, we use I_{ON} at a constant V_{GS} overdrive from the forward sweep ($V_{GS} - V_{TH,FWD} = -10$ V) and take I_{OFF} as the minimum I_{DS} from the same transfer curve to calculate the I_{ON}/I_{OFF} ratio. For devices with $V_{TH,FWD} < -5$ V, I_{DS} at $V_{GS} = -15$ V is used as I_{ON} , and the constant V_{GS} overdrive between $V_{GS} = -15$ V and $V_{TH,FWD}$ is used for both before and after metal deposition cases. This approach compares all devices at similar charge densities and reduces variability due to V_{TH} shift, and thus allows for a better comparison of performance across different devices.⁶ For devices with I_{OFF} lower than the measurement limit, the I_{OFF} was found by averaging currents in the regions with fluctuations in the off state below V_{TH} .

In order to test the stability of the improved junctions with time, we measured the transfer characteristics of our devices after operating them in air. The blue curve in Figure S2a shows the transfer curve after the device was exposed to air for two days. After another day, current was passed to this device with $V_{\text{DS}} = 5$ V and $V_{\text{GS}} = -15$ V for 10 seconds and the transfer characteristics was measured again (see red curve). We have noticed no noticeable difference between the two measurements, and used only the black and red curves in the main text in Figure 3b as before and after nanosoldering experiment data. Figure S2b shows how this device was converted to n-type after oxygen removal in vacuum, and how the performance was improved by nanosoldering while the device remained in vacuum.



Figure S2. (a) In-air transfer characteristics of the device in Figure 3a in the main text. (b) In-vacuum transfer characteristics of the device in Figure 3a in the main text. To further test the stability of our nanosoldering technique, current was passed to one of our nanosoldered devices for more than 20 hours. Figure S3 shows the current throughout the time period the device was under operation, and the inset plots show 10 transfer characteristic curves measured before and after the 20-hour current pass. The stable current during the device operation and consistent transfer curves show that our technique does not cause any stability issues related to possible electromigration and oxidation.



Figure S3. Time-dependence measurement of a nanosoldered device with $V_{DS} = 1$ V and $V_{GS} = -15$ V showing stable current over a 20-hour interval. The inset plots show consistent transfer curves before (left) and after (right) the 20-hour current flow treatment. Each plot is composed of 10 transfer curves measured consecutively.

For control experiments, CNT devices of similar network and crossbar geometries were used. These control devices were prepared in the same way; the devices were annealed at 600 K to remove oxygen molecules in vacuum,⁷ treated with similar current flow methods but in the absence of precursors, and exposed back to air for sufficient time (over 24 hours) to assess any changes in their transfer characteristics. Figures S4a summarizes the degree of improvement in the I_{ON}/I_{OFF} ratio ($I_{ON}/I_{OFF,AFTER} / I_{ON}/I_{OFF,BEFORE}$) for these devices, along with the devices nanosoldered with HfB₂ and Pd. As can be seen in the figure, the performance of control devices remained about the same or even degraded, possibly due to decreased channel and CNT-electrode contact resistances from the heat generated during the current passing through the device. The heat generated from this current anneal may cause the elimination of contaminants in CNTs and may also thermally anneal the contacts. The decreased channel and contact resistances can increase both I_{ON} and I_{OFF} and lower the overall I_{ON}/I_{OFF} ratio. The degree of decrease in these resistances may vary from device to device and from different batches of devices.

As noted in the main text, an improvement in the I_{ON}/I_{OFF} ratio of ~2.4 was observed in one of our control devices (indicated by green dotted circle in Figure S4a). Figure S4b shows an SEM image of this device. Note that during the control experiment, V_{GS} was set at 15 V and V_{DS} was applied from 5 V to 40 V for both current paths between Source 1 & Drain 1 and Source 2 & Drain 2. Figure S4c shows the transfer characteristic curve between Source 1 & Drain 1 before and after the control experiment. After noticing changes in the I_{ON}/I_{OFF} ratio, we put this device back into CVD chamber, and performed nanosoldering with the Pd precursor using the same conditions. Note that current was only passed between Source 2 & Drain 2 (electrodes falsecolored in red in the SEM image), and no current was passed between Source 1 & Drain 1. Then the measurements were made again using Source 1 and Drain 1 electrodes. By doing so, we were able to nanosolder the junctions and improve the I_{ON}/I_{OFF} ratio by another factor of ~8.25 (green dotted circle near right edge of Figure S4a). For AFM analysis on this device, refer to Figure S5 in the next section.



Figure S4. (a) Summary of improvement in I_{ON}/I_{OFF} ratios upon control experiment (black), HfB₂ deposition (red), and Pd deposition (blue). Points marked with * symbol corresponds to CNN devices and points marked with + symbol corresponds to CNT crossbar devices. (b) SEM image of a device indicated by green dotted circle in (a) before the control experiment. For the control experiment, current was passed between the source and drain of both red and blue electrodes. For Pd deposition, current was passed only between the red electrodes. (c) (Left) linear and (right) log scale transfer characteristics of the device in (b) measured between blue electrodes before and after the control experiment and Pd deposition.

4. Verification of Pd Deposition on CNTs

Atomic force microscope (AFM) images were collected using a Bruker Dimension IV AFM in tapping mode. The scan size was kept under 5 μ m × 5 μ m with a scan rate of 1 Hz. The resolution was 1024 × 1024. The drive amplitude and set point were carefully monitored to ensure good tracking of the surface. Figure S5a shows an SEM image of a CNT crossbar device before the control experiment and Pd deposition as discussed in the previous section. After the control experiment, current was passed between the red electrodes only and the electrical measurements were made using the blue electrodes (see Figure S4c). Figure S5b shows AFM images corresponding to the yellow dotted box in the SEM image before and after Pd deposition. The line scans along a CNT in dotted boxes (blue and red for before and after, respectively) show that sub-10 nm Pd particles were deposited at the junctions. We also note some Pd deposition along some other parts of CNTs, which may be defective sites.



Figure S5. (a) SEM image of a device indicated by the green dotted circles in Figure S4a before the control experiment. **(b)** AFM images corresponding to the yellow dotted box in (a) before (left) and after (right) Pd deposition, showing Pd particles of sub-10 nm size at the junctions. The bottom plots show height profiles along the CNT shown in the dotted boxes in the AFM images. **(c)** SEM image of a crossbar CNT device after intentional overdeposition of Pd. Current was passed between the two red false-colored electrodes. Green circles indicate where the EDS spectra in (d) were obtained. Scale bar is 5 μ m. **(d)** EDS spectra from Spot 1 (red) and Spot 2 (blue) verifying the presence of palladium.

In order to perform chemical analysis to verify the presence of Pd, EDS was performed on another device where high current was passed deliberately to deposit a large amount of Pd. Figure S5c shows an SEM image of such a crossbar CNT device after intentional overdeposition of Pd. Figure S5d shows EDS spectra from two different spots indicated by green circles in Figure S5c. EDS measurement from Spot 1 shows a Pd peak while the measurement from other parts of CNTs on the same device (Spot 2) does not show any noticeable Pd peak. The same measurement conditions were used for both cases and both plots are on the same scale.

5. Energy Dispersive X-ray Spectroscopy (EDS) for Boron

EDS analysis was performed using a FEI XL-30 SEM with field emission gun (FEG) source. Figure S6a shows SEM images of CNNs after HfB_2 deposition. Note that since boron is a light element, a CNT device with over-deposited HfB_2 is used for EDS. Spot 1 in the upper image of Figure S6a denotes the area where EDS spectrum (red curve) shown in Figure S6b was obtained. Spot 2 in the lower image of Figure S6a corresponds to CNN in the same device with no HfB_2 deposition, and the corresponding EDS spectrum (blue curve) is shown in Figure S6b. Note that the same acquisition conditions were used for both cases, and the two curves are on the same scale. The EDS data indicate that the deposited material indeed contains boron and the obtained boron spectrum is not simply from physisorbed precursor on the CNN.



Figure S6. (a) SEM images of (top) CNT network (CNN) with over-deposited HfB_2 and (bottom) CNN in the same device with no deposition of HfB_2 . Green circles indicate the spots where energy dispersive X-ray spectroscopy (EDS) spectra shown in (b) were obtained. Scale bar is 2 μ m. (b) EDS spectrum from spot 1 (red) and spot 2 (blue) verifying the presence of boron.

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