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

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Supporting Information

ABSTRACT: The performance of carbon nanotube network (CNN) devices is usually limited by the high resistance of individual nanotube junctions (NJs). We present a novel method to reduce this resistance through a nanoscale chemical vapor deposition (CVD) process. By passing current through the devices in the presence of a gaseous CVD precursor, localized nanoscale Joule heating induced at the NJs stimulates the selective and self-limiting deposition of metallic nano-solder. The effectiveness of this nanosoldering process depends on the work function of the deposited metal (here Pd or HfB2), and it can improve the on/off current ratio of a CNN device by nearly an order of magnitude. This nanosoldering technique could also be applied to other device types where nanoscale resistance components limit overall device performance.

KEYWORDS: Carbon nanotubes (CNT), nanosoldering, intertube junctions, electrical resistance, thermal resistance, local chemical vapor deposition (CVD)

Single-walled carbon nanotubes (CNTs) can be thought of as one-dimensional cylinders of monolayer graphene. Semiconducting CNTs exhibit high carrier mobility,1,2 and band gaps which vary inversely with diameter,3 whereas metallic CNTs can carry very high current densities.4 These properties make CNTs promising candidates as components in nanoelectronics.5,6 However, as-grown CNTs are a mixture of metallic and semiconducting types, which often hinders their practical applications. For instance, such mixtures do not have sufficiently high on/off current (I_{on}/I_{off}) ratios for low-power transistors, nor are they sufficiently metallic (i.e., independent of doping or gating) to act as interconnects. To address this challenge, there have been numerous attempts to eliminate metallic CNTs through electrical breakdown,7,8 diazonium functionalization,9,10 selective plasma etching,6,11 or by polymer wrapping and CNT sorting through ultracentrifugation.12 However, these methods require several postsynthesis processing steps that tend to contaminate or degrade the quality of the CNTs.

An alternative approach is to find ways to enhance the performance of random networks of as-grown carbon nanotube networks (CNNs). Such networks are easy to fabricate and transfer to arbitrary substrates, which make them attractive for applications in integrated circuits and display drivers on flexible or transparent substrates, especially because CNNs have shown higher carrier mobility than organic or amorphous silicon thin-film transistors.13,14 Sun et al13 have recently improved the performance of CNN devices through control of the CNN morphology and have achieved I_{on}/I_{off} ratios of \sim 10^6 and carrier mobilities of \sim 20 cm^2 V^{-1} s^{-1}. One of the challenges associated with CNNs is that the performance and reliability may be limited by high electrical15–19 and thermal20–23 resistances of CNT–CNT internanotube junctions (NJs). Such resistances depend on the CNT–CNT separation and overlap, which affect the hopping probability of charge carriers and consequently the junction resistances.18,19 From an electrical point of view, the current transport is further limited by Schottky barriers at the junctions between metallic and semiconducting CNTs.24,25 These junction resistances are at least an order of magnitude higher than those of individual CNTs.15–17 Thus, local power dissipation at these junctions will dramatically degrade the overall device performance.21,26 To address this issue, several studies have sought to improve the junction resistance by depositing metal particles at the NJs using electron beam induced deposition27 and dip-pen nanolithography facilitated by atomic force microscopy (AFM).28 While elegant, these methods are slow, requiring one to locate individual junctions to deposit metal nanoparticles in a serial fashion. Other studies have shown improvements in the sheet resistance of CNNs by employing selective nucleation of fullerences at the NJs29 and by treating CNNs with nitric acid and doping both the CNTs and the

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However, the details of these improvements in terms of electronic properties specific to transistor applications, such as mobility and $I_{ON}/I_{OFF}$ ratio, remained unexplored.

Recent transport studies of CNNs have shown that, during device operation, the temperature rise of the NJs is significantly higher than the average device temperature. These findings indicate that nanoscale hot spots form at NJs throughout the CNN (Figure 1a), a conclusion that is supported by recent simulations. In this study, we utilize these nanoscale hot spots to locally deposit metals via chemical vapor deposition (CVD). The net result is nanosoldering the NJs, which reduces their resistance and improves the overall CNN device performance.

We use test devices with two different geometries in our experiments, large area CNNs and CNT crossbar devices, as shown in Figure 1b. The CNNs were grown by CVD of methane gas with ferritin catalysts on SiO$_2$ (90 or 300 nm) with a highly doped Si substrate, which acts as a global back-gate. For CNT crossbar devices, aligned CNTs were initially grown on quartz substrates by CVD methods described elsewhere and subsequently transferred onto SiO$_2$ (200 nm) with a highly doped Si substrate at orthogonal directions to achieve well-defined NJs. Figure 1c shows schematic illustrations of the preparation of the CNT crossbar devices. Standard photolithography and electron beam evaporation were used to define metal electrodes; the latter consisted of 0.5 nm Ti (an adhesion layer for the SiO$_2$ substrate) topped with 40–80 nm Pd, which forms ohmic contacts to CNTs, owing to its high work function and favorable interaction with CNT sidewalls. Individual devices were then wirebonded to metal leads of a chip carrier. Additional details about our device fabrication can be found in our previous papers and in the Supporting Information.

In order to perform nanoscale CVD and nanosolder the NJs, entire samples were first loaded and kept in a vacuum chamber (~$10^{-6}$ Torr or lower) for several hours. Figure 2a shows the process flow for nanosoldering the NJs and Figure 2b shows the schematic diagram of our vacuum system for the CVD reactions. The samples were vacuum annealed at 600 K for five minutes to desorb oxygen molecules from the CNTs and the metal electrodes. Oxygen removal lowers the contact work function, causing conversion to n-type behavior in high vacuum. This change for our devices before and after oxygen desorption is shown by the transfer characteristics ($I_{DS}$ versus $V_{GS}$ with $V_{DS} = 50$ mV) and band diagrams in Figure 2c. After the samples were vacuum annealed and cooled to room temperature, the individually wirebonded devices were additionally heated by applying various voltages between the source and drain electrodes, thereby passing currents through the CNT devices to desorb all remnant oxygen molecules. These additional heating steps were repeated until there was no discernible change in the transfer characteristics of the devices. The oxygen removal step is carried out in order to clearly observe any change in the current transport in our device that may arise from nanosoldering the NJs. After the transfer
 characteristics stabilized, the background pressure of the CVD chamber was about 1–5 × 10⁻⁶ Torr.

Once the pressure in the CVD chamber stabilized, a single-source CVD precursor, either C₅H₅PdC₃H₅ or Hf(BH₄)₄, was introduced into the chamber until a total pressure of about 10⁻³ Torr was achieved to deposit Pd and metallic HfB₂,⁴₃,⁴₄ respectively. The approximate CVD reactions of each precursor are given by the following equations:⁴₃,⁴₅

\[
\begin{align*}
\text{C}_5\text{H}_5\text{PdC}_3\text{H}_5 (g) & \rightarrow \text{Pd} (s) + \text{C}_5\text{H}_5\text{C}_3\text{H}_5 (g) \quad (1) \\
\text{Hf(BH}_4)_4 (g) & \rightarrow \text{HfB}_2 (s) + \text{B}_2\text{H}_6 (g) + 5\text{H}_2 (g) \quad (2)
\end{align*}
\]

Because the precursors are air sensitive, they were kept in sealed stainless steel and glass containers under argon and stored in an ice bath or in a refrigerator at -20 °C until use. Both precursors have relatively high-vapor pressures (~30 Torr at 25 °C for C₅H₅PdC₃H₅ and ~15 Torr at 25 °C for Hf(BH₄)₄).⁴₃,⁴₆

After introduction of the precursors into the chamber, we varied the applied voltages over specific time periods to deposit Pd or HfB₂ at the locally heated NJs. Note that positive VDS was used while varying VGS in order to pass a high current because devices are now n-type. The ION/IOFF ratios were subsequently measured to monitor changes resulting from metal deposition. Finally, the samples were removed from the vacuum system and exposed to the ambient atmosphere for sufficient time (over 24 h) to allow readsorption of oxygen molecules. The ION/IOff ratios were again measured to assess the effects of nanosoldering the NJs on the p-type characteristics of the devices. In order to calculate the ION/IOFF ratio, we take ION at a constant VGS overdrive from the forward sweep (VGS - VTH,FWD = -10 V) and take IOFF as the minimum IDS from the same transfer curve (see Supporting Information) in order to better compare performance of different devices by comparing them at similar charge densities and to reduce variability due to VTH shift.⁴⁷ Note that for devices with IOFF lower than the measurement limit, the IOFF was found by averaging currents in the regions with fluctuations in the off state below VTH.

Figure 3a shows scanning electron microscope (SEM) images of a CNT crossbar device with well-defined NJs before and after Pd deposition. The two false-colored electrodes in red were used to pass current through the CNTs and electrodes in blue were left floating. VGS was applied up to 15 V in order to “turn on” both metallic and semiconducting CNTs, and VDS was applied from 5 to 35 V for three seconds. Figure 3b shows the transfer characteristic curves before and after Pd deposition for the device shown in Figure 3a. These results indicate that the ION was improved by a factor of ~6, while the IOFF (averaged in the regions indicated by black arrows) was lowered by a factor of ~1.42, leading to ION/IOFF ratio improvement by a factor of ~8.52. We also note that there was no significant effect on the threshold voltage hysteresis (ΔVTH,FWD - VTH,REV = 0.015 V), suggesting that Pd nanosoldering does not introduce new trap states near the CNT-SiO₂ interface. Thus, if we assume the current paths between source and drain electrodes remain unchanged (at a constant VGS overdrive) before and after Pd deposition, the improvement in ION is indicative of an increase in the average device mobility by a factor of ~6. Please refer to Figure S2b in

![Figure 2. (a) Process flow for nanosoldering NJs. (b) Schematic diagram of vacuum system for our nanoscale CVD process. (c) Transfer characteristics of a CNN device (left) in air and (right) in vacuum after oxygen removal steps from the device. The arrows indicate the VGS sweep direction. Corresponding energy band diagrams at the metal–CNT interface are shown in the insets of each graph. The left inset depicts hole injection into the CNT when a high work function metal, like Pd, contacts the CNT and the device is operated in air. The right inset depicts electron injection into the CNT when the oxygen molecules are desorbed off the metal surface and CNTs in vacuum and VGS > 0 V is applied (n-type behavior).](dx.doi.org/10.1021/nl4026083)
We attribute the increase in $I_{ON}$ to higher charge carrier hopping probability at the NJs, and thus lowered junction resistance. As Pd is deposited at the NJs, the area available for carrier flow is increased and the energy barrier is lowered. The decrease in $I_{OFF}$ may result from a heightened Schottky barrier for electrons in the off state. Figure 4 shows the schematic band diagrams for nanosoldered NJs between semiconducting CNTs, metallic CNTs, and semiconducting-metallic CNTs. In the devices we studied, Pd is used for both the source and drain electrodes, and the CNTs form percolation paths between the two electrodes. CNT contacts to Pd electrodes induce p-type behavior at the source and drain because Pd has a high work function ($\Phi_{Pd} = 5.1-5.9$ eV). Therefore, nanosoldering the NJs with Pd will also induce p-type behavior at these NJs, and the lowered Schottky barrier at the valence band edge and increased Schottky barrier for electrons in the off state will lead to a large improvement in the overall device performance. We note that even though a large improvement in the $I_{ON}/I_{OFF}$ ratio was observed, we did not find any large Pd particles after nanosoldering. Instead, a slight increase in contrast along some CNTs near the NJs was observed after Pd deposition as can be seen in Figure 3a. The right-hand images are magnified views of the region indicated by the yellow dotted box, before and after Pd deposition. We speculate that only a very small amount of Pd is needed to connect the CNTs at the NJs because Pd is known to wet CNTs very well\textsuperscript{51,52} Once these NJs are soldered, their resistance decreases and they cool, thus stopping the nanosoldering process.

In order to confirm that Pd was deposited on the NJs, the nanosoldering was deliberately carried out with high currents for longer times (up to 30 s) on other similar devices to deposit a larger amount of Pd. Post characterization with SEM and AFM (see Figure S5 in Supporting Information) indicate that Pd nanoparticles from sub-10 nm to over 30 nm in size were deposited on the NJs. The deposited material was also verified to be Pd by elemental analysis using energy dispersive X-ray spectroscopy (EDS).

Additional control experiments were performed on similar crossbar and CNN devices that were annealed in vacuum and subjected to the similar set of deposition conditions without actually introducing any precursor into the chamber. These experiments allowed us to test the possibility that the improvement in device performance was due to factors other than nanosoldering. For a majority of devices we tested, the $I_{DS}-V_{GS}$ characteristics remained about the same or even degraded after these control experiments (see Supporting Information). On a single device, we saw an $I_{ON}/I_{OFF}$ ratio improvement of a factor of $\sim 2.4$, possibly due to the elimination of contaminants on CNTs or thermal annealing.
of the contacts from the heat generated during current flow. However, we were able to nanosolder this same device with Pd after the control experiment and improve the $I_{\text{ON}}$ by a factor of $\sim 5.9$ while decreasing the $I_{\text{OFF}}$ by a factor of $\sim 1.4$, leading to the overall performance improvement of another factor of $\sim 8.25$ (see Supporting Information). Notably, we have not observed any device for which $I_{\text{OFF}}$ decreases after a control experiment conducted without the CVD precursor. Thus the decreased $I_{\text{OFF}}$ after Pd deposition in our devices suggests that nanosoldering Pd is indeed playing a role at the NJs. In order to test the stability of the improved junctions with time, we also performed time-dependence measurements in which current was passed through one of our nanosoldered devices for more than 20 h (see Figure S3 in Supporting Information). The stable current during the device operation and consistent transfer curves in Supporting Information Figure S3 show that our technique does not suffer from stability issues such as electromigration or oxidation.

In order to clarify the effect of the nanosolder work function, we then used the precursor Hf($\text{BH}_4$)$_4$ to deposit HfB$_2$ at the NJs. We chose the precursor Hf($\text{BH}_4$)$_4$ because the resultant HfB$_2$ has a high melting point (3250 °C) and excellent electrical properties, a resistivity of $\sim 15 \ \mu\Omega\text{-cm}$ and a low work function ($\phi_{\text{HfB2}} \approx 3.5 \ \text{eV}$). Figure 5a shows SEM images of a CNN device before and after HfB$_2$ nanosoldering. The bright islands in the figure indicate that HfB$_2$ has been deposited primarily at crossed NJs. We also note that a few CNTs are coated with HfB$_2$ along almost their entire lengths, vividly highlighting the most conductive current pathways that heat up during device operation. EDS measurements confirm the presence of hafnium: the red curve in Figure 5b shows the EDS spectrum obtained from a bright island formed at a NJ, whereas the blue curve shows the EDS spectrum obtained from CNTs in the same device away from the bright island under the same acquisition conditions. Data regarding the presence of boron are provided in the Supporting Information.

Figure 6a shows SEM images of another CNN device before and after HfB$_2$ deposition. The yellow circles indicate regions where HfB$_2$ was deposited on the NJs. Figure 6b shows the transfer characteristics of this device before and after HfB$_2$ deposition where the $I_{\text{ON}}$/$I_{\text{OFF}}$ ratio was improved by $\sim 24\%$ using our nanosoldering technique. Note that there was little change on the threshold voltage hysteresis ($\Delta V_{\text{TH,FWD}} - V_{\text{TH,REV}} = 0.23 \ \text{V}$), suggesting that HfB$_2$ nanosoldering does not introduce new trap states. We tested several other devices with similar channel geometries, as well as CNT crossbar devices, and found the device performance either showed less improvement or could even be degraded (see Supporting Information for more data). We believe that the difference in the work function of the electrode metal, Pd, and the deposited metal, HfB$_2$, plays a role here. When a low work function metal comes in contact with a semiconducting CNT, charge transfer occurs from the metal to the CNT and creates a Schottky barrier at the valence band edge, inducing n-type behavior at the contact as shown in Figure 4. Therefore, when the NJs are nanosoldered with HfB$_2$, n-type behavior is induced in the middle of the CNT percolation paths between the source and drain electrodes, while p-type behavior is induced at CNT contacts to the source and drain electrodes because Pd has a high work function. This mismatch of work functions will create back-to-back pnp junctions within the CNN for HfB$_2$ nanosoldered junctions, which can degrade the current transport of the device. We also note that, unlike the Pd case, large HfB$_2$ particles were visible after nanosoldering the junctions (see Figures 5 and 6). We believe that when HfB$_2$ is deposited at these NJs, the resistance will not drop as much due to the work function mismatch and the poor interface between HfB$_2$ and CNTs (compared to Pd which wets CNTs very well) and thus the nanosoldering process will continue, making much larger islands. Figure 6c shows a histogram that summarizes the degree of improvement in the $I_{\text{ON}}$/$I_{\text{OFF}}$ ratio ($I_{\text{ON}}/I_{\text{OFF, AFTER}} / I_{\text{ON}}/I_{\text{OFF, BEFORE}}$) for the control, HfB$_2$-deposited, and Pd-deposited devices. For more details on these devices, please refer to Figure S4 in Supporting Information.

In conclusion, we achieved nanoscale CVD of metallic nanoparticles at NJs by passing current through devices like CNNs and CNT crossbars to selectively heat the NJs. This process results in self-aligned and self-limiting nanosoldering that reduces the junction resistance and improves the device transport properties. By matching the work function of the electrode with the metallic nanosolder (e.g., by using Pd), we improved the $I_{\text{ON}}$/$I_{\text{OFF}}$ ratio of our devices by nearly an order of magnitude. The self-limiting nature of the nanosoldering process means that the NJs cool as they are soldered, and the next most-resistive NJs will undergo nanosoldering. The nanosoldering technique may be generally applicable to improve the performance of other materials and devices.

![Figure 5](dx.doi.org/10.1021/nl4026083) Nano Lett. 2013, 13, 5844–5850
ASSOCIATED CONTENT

Supporting Information
We include fabrication of CNT devices, sample preparation and experimental setup, control experiments and additional data analysis on reliability and vacuum measurements, verification of Pd deposition on CNTs, and energy dispersive spectroscopy (EDS) data for boron. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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Figure 6. (a) False-colored SEM images of a CNN before (left) and after (right) HfB2 deposition. Yellow circles are used to indicate NJs where HfB2 was deposited. (b) Linear (left) and log (right) scale transfer characteristics of the CNN device before and after HfB2 deposition with VDS = 50 mV. The arrows indicate VG sweep direction. Note that the measurement in (b) was made before SEM imaging and the breaking of CNTs near the source in (a) was caused by electrostatic discharge during handling after the measurement. (c) A histogram showing the improvement in ION/IOFF ratios upon control experiment (black), HfB2 deposition (red), and Pd deposition (green).