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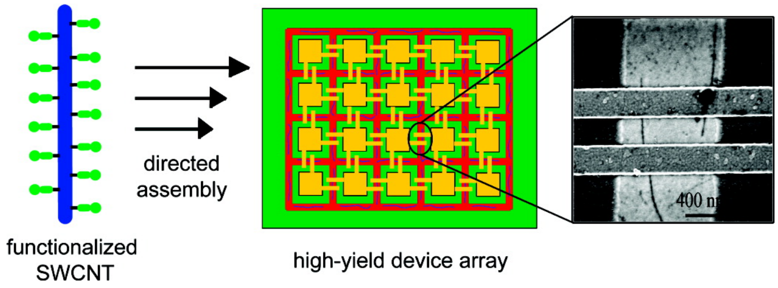

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Chemically Assisted Directed Assembly of Carbon Nanotubes for the Fabrication of Large-Scale Device Arrays

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Abstract: We report the directed assembly of single-walled carbon nanotubes (SWCNTs) at lithographically defined positions on gate oxide surfaces, allowing for the high yield (∼90%) and parallel fabrication of SWCNT device arrays. SWCNTs were first chemically functionalized through diazonium chemistry with a hydroxamic acid end group that both renders the SWCNTs water-soluble and discriminately binds the SWCNTs to basic metal oxide surfaces (i.e., hafnium oxide (HfO_2)). The functionalized SWCNTs are then assembled from an aqueous solution into narrow trenches etched into SiO_2 films with HfO_2 at the bottom. The side walls of the patterned trenches induce alignment of the SWCNTs along the length of the trenches. Heating the structures to 600 °C removes the organic moieties, leaving pristine SWCNTs as evidenced by Raman spectroscopy and electrical measurements. Palladium source−drain electrodes deposited perpendicular to the trench length readily contact the ends of the aligned SWCNTs. The resultant devices exhibit the electrical performance expected for SWCNT devices, with no performance deterioration as a result of the placement process. This technique allows for the directed assembly and alignment of SWCNTs over a large area and results in a high yield of working devices, presenting a promising path toward large-scale SWCNT device integration.

Introduction

Single-walled carbon nanotubes (SWCNTs) are a promising emerging material for the continued scaling of logic circuits due to their excellent properties as the active channel in field-effect transistors.[1−5] To fully exploit their superior transport properties, fabrication tools need to be developed to address many substantial processing challenges such as their separation, chemical doping, and selective placement. This paper details a method for the selective placement of SWCNTs, via chemically assisted directed assembly, that allows for large area, high-yield fabrication of electronic devices. There are numerous reports on using patterned self-assembled monolayers (SAMs) to selectively place SWCNTs.[6−10] They rely on patterning SAMs, usually on SiO_2, with terminal functional groups that either promote or inhibit SWCNT adhesion. More recently, reports from this laboratory[11,12] have detailed a method to reversibly functionalize SWCNTs with compounds that selectively bind to patterned surfaces. The functionalized SWCNTs were dispersed in alcohol, dried onto the patterned surface, and then sonicated to remove the loosely bound functionalized SWCNTs. Although the process results in selective placement, the drying/sonication process could not produce orientation control or a high yield over a large area. Here, we were able to overcome these limitations by using chemistry that renders the SWCNTs water-soluble, allowing for control over the subtle acid−base surface reactions via carefully modifying the pH. The functionalized SWCNTs can simply diffuse to the surface in the aqueous solution and bind to the surface reaction sites leading to alignment and large-area assembly.

The important results of this work are that the precise location and orientation of water-soluble chemically functionalized SWCNTs can be controlled, allowing for the fabrication of large device arrays in a high yield. The process is illustrated in Figure 1. The SWCNTs are first modified with organic compounds that are end-functionalized with organic acids (hydroxamic acids) that impart water solubility and selectively bind to basic metal oxides, exemplified in this study by hafnium oxide (HfO_2), a technologically important high-κ gate oxide. Substrates are fabricated with narrow trenches etched through the top SiO_2 layer (in green in Figure 1) of a SiO_2 on HfO_2 (in red in Figure 1) gate dielectric stack. Immersion of the patterned substrates in functionalized SWCNT (f-SWCNT) solutions directs the assembly of the f-SWCNTs onto the HfO_2 surfaces, forming

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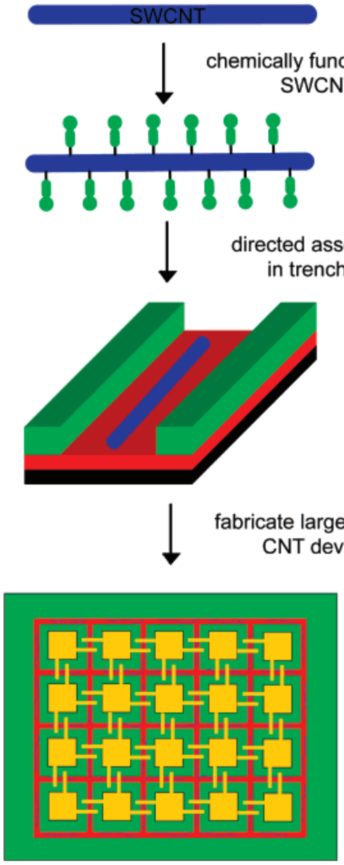


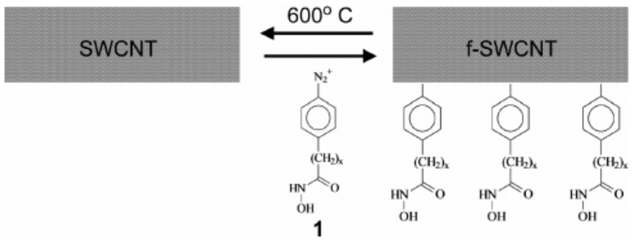
Figure 1. Overview of the directed assembly method used to create large arrays of SWCNT devices. The process includes chemical functionalization, assembly, and alignment of functionalized nanotubes into arrayed trench structures followed by parallel device fabrication. HfO_2 trenches are in red, SiO_2 layer is in green, and top metal source−drain electrodes are in yellow.

the bottom of the trenches. The trench sidewalls induce alignment of the f-SWCNTs along the length of the trenches. The patterned substrate is then gently rinsed with water to remove any functionalized tubes from the SiO_2 areas. The SWCNT modification is then reversed via annealing at 600 °C in argon, to leave pristine nanotubes behind. A Ti/Pd source−drain electrodes are deposited orthoganol to the trench length to fabricate large arrays of many SWCNT devices in parallel with high yield. The resulting devices showed typical SWCNT device characteristics, with no deterioration of the device properties as a result of the processing. The method provides a promising path for the integration of SWCNTs into logic devices.

Experimental Procedures

***O*-Benzyl 4-Nitrophenylhydroxamic Acid (2)**. Oxalyl chloride (10.16 g, 0.08 mol) was added to a solution of 4-nitrobenzoic acid (6.68 g, 0.04 mol) in 100 mL of anhydrous dichloromethane. A drop of *N*,*N*-dimethylformamide was added, and the mixture was stirred under nitrogen for 3 h. The solvent and excess oxalyl chloride were evaporated under reduced pressure. The residual oily compound was redissolved in 20 mL of anhydrous dichloromethane and added to a solution of *O*-benzylhydroxylamine hydrochloride (0.04 mol) and triethylamine (0.08 mol) in 50 mL of anhydrous dichloromethane. The mixture was stirred at room temperature for 4 h and then washed with dilute hydrochloric acid and brine, dried over anhydrous magnesium sulfate, and filtered. Evaporation of the solvent gave a light brown solid, which was crystallized from ethanol to give *O*-benzyl-4-nitrophenylhydroxamic acid as white crystals (7.9 g, 73%), mp 169−170 °C. NMR ($CDCl_3$); 5.03 , s 2H; 7.4−7.55, m 5H, 7.93 d, $J = 7$ Hz, 2H, 8.31 d, $J = 7$ Hz, 2H.

Scheme 1



4-Aminophenylhydroxamic Acid (3). Palladium on activated carbon (10%, 500 mg) was added to a mixture of *O*-benzyl 4-nitrophenylhydroxamic acid (2.71 g, 0.01 mol) and ammonium formate (3.65 g, 0.05 mol) in 100 mL of anhydrous methanol, and the solution was refluxed under nitrogen for 4 h. The hot mixture was filtered, and the solvent was removed under reduced pressure. The residual solid was crystallized from water to give 4-aminophenyl hydroxamic acid (1.18 g, 78%) as white needles, mp 144−145 °C. NMR (CD_3OD); 6.62 d, $J = 6$ Hz, 2H and 7.65 d, $J = 6$ Hz, 2H.

In Situ Functionalization of SWCNTs. Nitrosonium tetrafluoroborate (118 mg, 1 mmol) was added to a suspension of 4-aminophenylhydroxamic acid (152 mg, 1 mmol) in 10 mL of anhydrous acetonitrile, and the solution was stirred under nitrogen for 30 min. The yellow diazonium (**1**) solution was then added to a dispersion of laser ablated carbon nanotubes (5 mg) in 100 mL of 1% aqueous sodium dodecylsulfonate (SDS), and the mixture was stirred for 2 h. The mixture was diluted with acetone (5×) and centrifuged at 3600 rpm for 25 min. The supernatant liquid was discarded, and the precipitated SWCNTs were dissolved in water by sonication to form a stable aqueous solution of functionalized SWCNTs.

Characterization. Raman spectroscopy was performed on pristine laser ablated SWCNTs, f-SWCNTs, and annealed (defunctionalized) SWCNTs. The samples were prepared by drop casting an acetone dispersion (for pristine SWCNT) or a water dispersion (for f-SWCNT) of the corresponding nanotubes onto a 1 in. diameter, optically flat sapphire window followed by drying the solution over a stream of nitrogen. The 488 nm line from a Coherent Ar-ion laser was used as the excitation beam, and the back-scattered radiation was analyzed with a Jobin-Yvon monochromator, equipped with a 1200 groves/mm grating blazed at 500 nm, in combination with a liquid nitrogen cooled CCD camera. The Raman data were calibrated to the sapphire peaks from the substrate.

The device fabrication began with atomic layer deposition (ALD) of 2.5 nm hafnium oxide (HfO_2) onto a heavily doped silicon wafer. Silicon oxide (20 nm) was then thermally grown on top of the HfO_2 layer at low temperatures to prevent diffusion. Electron beam lithography was used to define an integrated array of trenches in a PMMA resist layer. SiO_2 was etched away by 30 s immersion in a commercially available 9:1 Buffered Oxide Etch (Fisher Scientific) composed of an aqueous NH_4−HF solution, exposing the underlying HfO_2 at the bottom of the trenches. The substrates were rinsed in deionized water, followed by an oxygen plasma treatment. The sample was then placed in an aqueous dispersion of SWCNTs modified with **1** to assemble the tubes in the trenches. The devices were annealed at 600 °C for 120 s in argon to remove the surface functionality and completed by e-beam evaporation of source−drain electrodes oriented perpendicular to the trench length. The electrical characteristics where measured with a probe station and parameter analyzer (Hewlett-Packard 4156).

Results and Discussion

The chemistry employed to carry out the functionalization and directed assembly is highlighted in Scheme 1. The diazo-

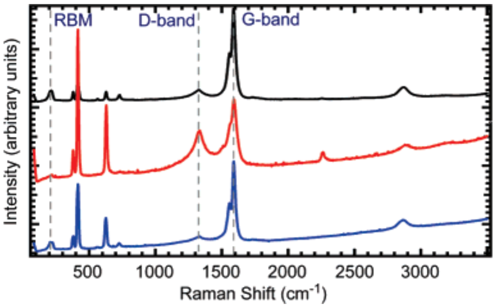


Figure 2. Raman spectra of pristine SWCNT (black trace), after functionalization with **1** (red trace), and after annealing to remove **1** (blue trace). The data were acquired by depositing the samples onto sapphire windows and using a 488 nm excitation.

nium salt (**1**) reacted readily with SWCNTs to yield the functionalized species (f-SWCNT). The diazonium salt formed a charge-transfer complex at the surface of the SWCNT with electron transfer from the SWCNT to the organic compound leading to the formation of a SWCNT-aryl carbon−carbon bond, converting the sp^2 hybridized SWCNT carbon atom to a sp^3 hybridized carbon atom.[13−17,22] Annealing the reacted material to 600 °C, under argon, cleaved the SWCNT-aryl bond, restoring the original sp^2 hybridization of the SWCNT. Compound **1** was end-functionalized with hydroxamic acid. Hydroxamic acids are known to bind strongly and selectively to basic metal oxides (i.e., Al_2O_3 and HfO_2) as opposed to silicon oxide.[12,18] We use a short-chain ($x = 0$) hydroxamic acid terminated compound that renders the functionalized SWCNTs water-soluble. An advantage of using aqueous solutions, as opposed to common organic solvents as used in the previous reports,[10,11] is that the solution pH can be precisely controlled to mediate the subtle acid−base interaction between the terminal hydroxamic acid and the desired metal−oxide surface allowing for increased SWCNT density and, subsequently, increased device yield. The SWCNT functionalization is completely reversible upon annealing to 600 °C. This reversibility is critical since the attachment chemistry rehybridizes the carbon atoms at the point of attachment, introducing scattering sites and severely degrading the SWCNTs device performance.

Raman spectroscopy is a powerful tool for probing the dynamics of SWCNT functionalization.[19,20] Figure 2 shows the Raman spectra, at 488 nm excitation, of pristine SWCNTs prior to any chemical treatment (black), of SWCNTs functionalized with **1** (red), and of f-SWCNTs annealed to 600 °C (blue). The pristine SWCNTs (Figure 2, black trace) show all the requisite peaks associated with typical Raman spectra of SWCNTs.[19,20] The radial-breathing mode (RBM), associated with the ring vibration perpendicular to the long axis of the nanotube, is assigned to the peak at ∼220 cm^{-1}, while the peaks at 1590 and 1570 cm^{-1} are assigned to the G$^+$ and G$^-$ bands, respectively, and are associated with the C−C stretch modes along the nanotube axis (G$^+$) and the circumferential direction (G$^-$). The D-band, 1350 cm^{-1}, is commonly referred to as the defect band and is a phonon mode activated by the presence of defects in the structure of the SWCNT. The peaks at 378, 417, and 645 cm^{-1} are assigned to the E_g and A_{1g} peaks of the sapphire substrate and were used to calibrate the spectra. Since the functionalization results in the hybridization of the bonded carbon atoms (from sp^2 to sp^3) of the SWCNTs, defects are introduced into the crystal structure upon functionalization, increasing the intensity of the D-band mode. Monitoring the intensity ratio between the D-band and the G-band, I_D/I_G, will indicate whether the reaction took place, to what degree, and if it was reversed. The I_D/I_G ratio is significantly higher in the spectrum taken of the functionalized SWCNTs (Figure 2, red trace). The G-band intensity is attenuated and broadened as well. This ratio reverts to the initial value upon annealing the functionalized SWCNTs, as is seen in the blue trace in Figure 2, suggesting that the SWCNTs are defunctionalized and that the sp^3 carbon atoms have rehybridized back to the sp^2 state. The RBM peak at 220 cm^{-1} also decays upon functionalization as the symmetry of the radial mode is broken due to covalent attachment of the organic moiety.[24] This mode is also fully recovered upon annealing. The data confirm that the SWCNTs are chemically functionalized with **1** and that the functionalization is reversible.

The hydroxoxamic acid functionality was chosen due to its ability to discriminate between basic metal oxides and silicon oxide surfaces.[12,18] Metal oxides with large isoelectric points (IEP) are able to deprotonate the weakly acidic hydroxamic acids (pK_a = ∼9.3), resulting in a hydroxamate ion that can more readily chelate to the oxide surface. Using the patterned substrates, the weakly bonding hydroxamic acid species exists at the acidic SiO_2 surface (IEP = ∼2), while the mostly deprotonated, strongly bonding hydroxamate species exists on the more basic HfO_2 surface (IEP = ∼8), leading to selective binding to the basic metal oxide surface. The pH can be carefully tuned to mediate this acid−base interaction to maximize the binding density, while keeping the functionalized tubes stably suspended. This, coupled with the high oxidation state of the hafnium ion (4+), leads to strong and selective binding of the f-SWCNTs to the HfO_2 surface. It is also important to note that using dielectrics deposited via atomic layer deposition (ALD) yielded a higher density than those deposited via electron beam deposition. ALD yields atomically smooth surfaces and therefore a more homogeneous surface structure. It is presumably this homogeneity that results in these superior results. To take advantage of the binding selectivity, substrates were lithographically patterned to expose HfO_2 channels for the placement of the modified SWCNTs, as illustrated in Figure 3a. Trenches of various line widths were fabricated by chemically etching the SiO_2 overlayer through a photoresist mask. The substrates were then exposed to a solution of the f-SWCNTs for 3 h, removed from the solution, and rinsed thoroughly with deionized water before being imaged with scanning electron and atomic force microscopes. The images (Figure 3b−d) reveal the functionalized carbon nanotubes assembled strictly in the region with exposed HfO_2. The rest of the surface, composed of SiO_2, was completely free of any f-SWCNTs.

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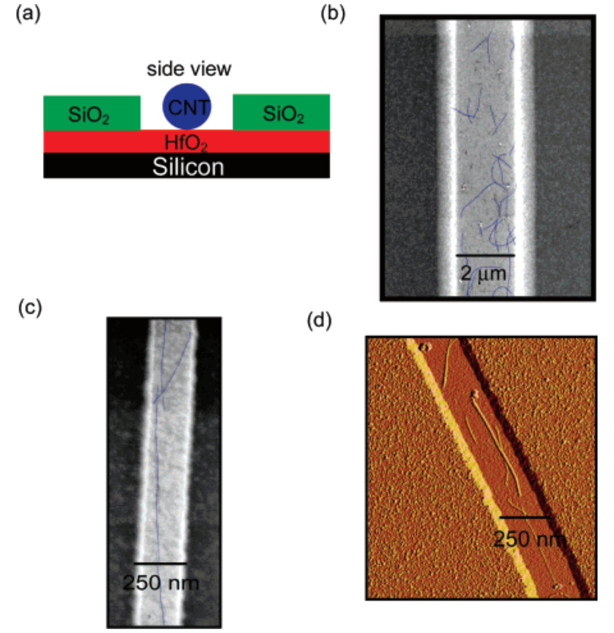

Figure 3. (a) Schematic of the side view of the patterned substrates. (b) SEM image of functionalized SWCNTs (in blue) assembled in a 2 μm HfO_2 bottomed trench. (c and d) SEM and AFM image, respectively, of 250 nm trenches with aligned functionalized SWCNTs inside the HfO_2 bottomed trenches.

As the width of the trench decreases (from Figure 3b), to below the average length of the nanotubes (Figure 3c,d), the tubes align along the length of the trench. Figure 3b is an SEM image of a 2 μm wide trench that was exposed to a solution of f-SWCNTs. The tubes assemble into the trench with a relatively high density (~2 SWCNT per μm^2); however, the tubes are oriented in random directions inside the trench. As the width of the trench becomes smaller than the average length of the f-SWCNTs, the tubes tend to align along the length of the trench. This is clear in both the SEM and the AFM images of Figure 3c,d, respectively. The side walls of the trench constrain the nanotubes to assemble in the orientation of the trench itself. This is crucial in the fabrication of electronic devices as either end of the assembled carbon nanotube can be easily contacted with source−drain electrodes deposited in a direction perpendicular to the trench length. The opposite geometry was also fabricated, where HfO_2 ridges are made on top of a SiO_2 substrate. In that geometry, the functionalized carbon nanotubes have a tendency to hang over the edge and onto the SiO_2 substrate, lacking any orientation control.[21]

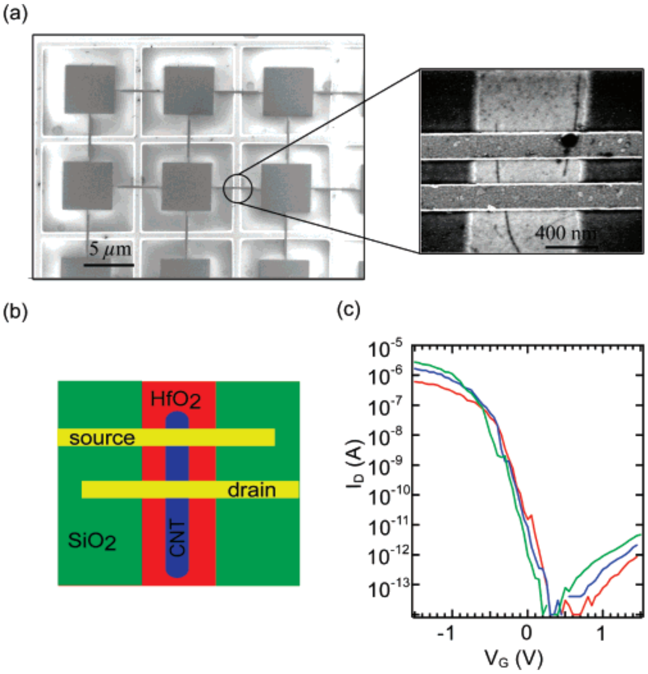

Figure 4. (a) SEM images of one section of the array structure and of a single device (inset) in the array with a single SWCNT spanning the source−drain electrodes. (b) Schematic of the top view of a single device. (d) I_D vs V_G curves for a typical device at $V_D = 0.1$ V (red trace), 0.3 V (blue trace), and 0.5 V (green trace).

The SWCNT density can be tuned by carefully adjusting the pH and varying the deposition time and the width of the trench, such that at any given point in the trench there is a high probability of finding one, and only one, SWCNT to electrically contact. Once these conditions were determined (pH = 6.5−6.9, 3 h deposition, width = 800 nm), large device arrays were fabricated using the trench geometry. Figure 4a illustrates a portion of a typical grid structure that consists of 40 source−drain pairs. The structures were fabricated by first making the large grid of trenches, followed by the directed assembly of f-SWCNTs into the trenches. The samples were then annealed to defunctionalize the SWCNTs, leaving the pristine SWCNTs behind. Source−drain electrodes (Ti/Pd) were then lithographically defined perpendicular to the trenches in a highly parallel fashion to achieve the structure shown in the SEM image. The inset of Figure 4a shows one device in the larger array. The source−drain electrodes cross the trench and are spaced by 300 nm, significantly less than the SWCNT length to ensure that the SWCNT spans the length of the source−drain pair. Since the source−drain electrodes run perpendicular to the trench, the alignment along the length of the trench was crucial to achieve a high yield. Images and transport measurements were taken of dozens of these device arrays, and approximately 90% of the source−drain electrode pairs had a single SWCNT spanning the contacts (>35/40 devices per array out of 8 arrays). Since the metallic SWCNTs react at a faster rate with the diazononium salts than the semiconducting SWCNTs, the resulting devices yielded an enrichment of metallic SWCNTs where 70% of the devices was metallic. By using a reported presorting process that separates semiconducting from metallic SWCNTs and coupling it to this placement process, viable logic circuits could be fabricated of strictly semiconducting SWCNTs.[22,23]

A representative I_D versus V_G curve of a contacted semiconducting SWCNT is shown in Figure 4c. The SWCNT is expectedly *p*-type with the drain current increasing as the gate voltage is swept in the negative direction with a constant source−drain voltage. The on-current is high, 1 μA, which is expected for SWCNT devices, and the on−off ratio was measured to be 10^7. These values are consistent with measurements for pristine carbon nanotubes with similar dielectric

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(21) See Supporting Information for images of substrates with inverted geometry and larger area images.

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thicknesses, diameters, and source−drain lengths, providing further evidence that the chemical functionalization is fully reversible. This method produced dozens of single SWCNT devices with no apparent performance deterioration as a result of the processing.

Conclusion

Chemical functionalization and directed assembly of SWCNTs is a powerful route for the fabrication of large-scale arrays of SWCNT devices. Organic acids impart water solubility to SWCNTs that allows the pH to be tuned to achieve selective and more precise placement of SWCNTs on patterned oxide surfaces having different isoelectric points. This method also allows for directed assembly into predefined positions of oriented SWCNTs by confining the SWCNTs to the trenches of patterned dielectric stacks. Large arrays of functioning SWCNT devices were fabricated in high yield and with the superior electronic properties expected of carbon nanotubes, with no deleterious effects on the electrical performance. The precision, ease, and resultant high yield of this method provide a promising route to the parallel fabrication of large-scale carbon nanotube electronics.

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Supporting Information Available: Images of assembled SWCNTs on different geometries and of larger areas. This material is available free of charge via the Internet at http://pubs.acs.org.

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