



**Solution Deposition Methods for Carbon
Nanotube Field-effect Transistors**

by Natalie Salaets and Matthew Ervin

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Sensors and Electron Devices Directorate, ARL**

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14. ABSTRACT This study evaluated different methods for controlled deposition of carbon nanotubes (CNTs) from solution onto a silicon substrate to make CNT field-effect transistors (FETs). The goal of this deposition was to achieve reproducible device properties through more uniform CNT densities and other traits. This method serves as an easier, room temperature alternative to chemical vapor deposition growth. Three different types of CNT solutions were spun onto substrates: pristine tubes solubilized with surfactant, COOH-functionalized tubes, and aminopyrene non-covalently functionalized tubes. Characterization of the CNT films was done with scanning electron microscopy. The CNTs were processed into FETs using standard microelectronics processing techniques. The resulting devices were characterized using a semiconductor parameter analyzer to measure their electrical properties. Preliminary results showed that the aminopyrene non-covalently functionalized CNTs were better dispersed and centrifugation could remove agglomerated tubes from the solution prior to spin-coating. A comparison of the results for each deposition method will help to determine which conditions are useful for producing CNT devices for chemical sensing and electronic applications.					
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1. Introduction and Background

1.1 Background

In 1991, scientists discovered a new form of carbon, a sheet of graphene rolled up into a one-dimensional tube. These carbon nanotubes (CNTs) have remarkable electrical and material properties, such as a very high aspect ratio and capabilities of being semiconducting or metallic depending on chirality (1). Semiconducting CNTs can carry high current densities, exhibit high on/off current ratios, and have high electron/hole mobilities (2). With such advanced properties, CNTs are being used extensively for research in electronic devices.

Extensive research has been done on carbon nanotube field-effect transistors (CNTFETs), which may revolutionize the electronics industry in the future. Single-walled carbon nanotubes (SWNTs) act as the channel between the source and the drain of the transistor device. CNTFETs can have very high on/off current ratios, but the presence of metallic CNTs, in addition to semiconducting CNTs, reduces the on/off ratio significantly. Therefore, the CNT thin film has a major influence on the transistor behavior and must be carefully developed.

There are three main challenges in achieving the most useful CNT films for CNTFET devices, all of which can be addressed with solution-based methods. Firstly, the chirality of the tubes, which has a direct effect on the electronic properties, can be sorted or controlled to produce mostly semiconducting SWNTs. Secondly, the tubes should have some degree of alignment rather than a randomly dispersed network. Thirdly, the tube density should be at a level adequate for a high device yield, yet low enough to minimize the effect of metallic SWNTs, which reduce the performance of CNTFETs.

Many solution-based methods studied have had similar issues with eliminating the metallic nanotubes from the CNT films. One group was able to achieve on/off ratios of more than 10^5 through manipulating surface functional groups on the substrates during spin-assisted assembly (3). Another group used an electrical breakdown procedure to remove metallic SWNTs and were eventually able to achieve on/off currents of up to 10^4 from their solution-processed thin film transistors (TFTs). They applied these TFTs to construct working logic circuits and hope to eventually use this technology for printable flexible electronics (4, 5). Other researchers have found a solution preparation method involving ultracentrifugation, sonication, and filtration of solutions prepared from SWNT powders, resulting in the removal of a significant portion of metallic SWNTs as verified by optical absorption, Raman measurements, and electrical measurements (2). Alternatively, research on SWNTs wrapped by single-stranded DNA, known as DNA-CNTs, has been done to obtain controlled patterns of spontaneously

aligned SWNTs (6). Yet another group used a tilt-drop casting technique to achieve highly oriented CNTs and specified how the inter-nanotube contact resistance of many overlapping tubes may limit the potential high carrier mobilities of SWNTs (7).

1.2 Motivation

The purpose of this research is to determine the most useful parameters for the controlled deposition of CNTs, optimized for the fabrication of CNTFETs. The main goal is to create CNTFETs with reproducible, predictable properties. Solution deposition serves as an alternative to the chemical vapor deposition (CVD) growth of nanotubes. It is faster and simpler, and can be conducted at room temperature, unlike CVD, which requires temperatures up to 900 °C (8). Ultimately, this process will help to increase nanoelectronic device manufacturability, enabling large-scale fabrication of CNT-based electronic devices. Deposition of CNTs from solution may also permit additional approaches to functionalizing CNTFETs to make sensors. This research on CNTFETs will eventually be used for chemical sensing and electronic applications valuable for the Army warfighter.

2. Experimental Methods

2.1 Solution and Sample Preparation

A total of three processing runs, which varied a number of process parameters, were completed for this study. The resulting CNT films were characterized to explore the reproducibility and uniformity of CNT films. The CNT solutions were initially acquired from NanoLab, Inc., with three different solution types: pristine SWNTs solubilized with surfactant, COOH-functionalized SWNTs, and aminopyrene non-covalently functionalized SWNTs with a dispersant. For each run, the devices were processed using the three solutions in parallel. A total of 22 samples were fabricated from these runs, which are summarized in table 1.

The solution concentrations were all originally 400 mg/L of CVD CNTs in acetone. Each solution was drawn from the main container with a dropper and put into a 10 mL vial. Some solutions were then diluted 10× or 100× with acetone. Next, the vials were sonicated in a Branson 2510 Ultrasonic bath at a frequency of 40 kHz for different lengths of time. The ultrasonic bath disperses the tubes throughout the solution so that the tubes are separated and debundled. After sonication, some solutions were centrifuged in an Eppendorf 5415D Centrifuge for varying lengths of time and at varying RPMs to settle out any remaining bundled nanotubes, leaving behind mostly individual single-walled nanotubes.

Table 1. Controlled spin deposition conditions for three processing runs, producing a total of 22 samples.

Processing Run #1											
Solution	Sample	Function- alization	Dilution	Bath Sonication Time (min)	Delay before Spin or Centrifuge	Centrifuge Time (min)	Centrifuge RPM	Spin Speed (RPM)	Spin Type	# of Drops	Pre-Test Processing
C3	C3.c	pristine	none	60	2 days	–	–	1000	Static	–	–
C4	C4.a	COOH	none	65	2 min	–	–	1000	Static	–	–
	C4.b	COOH	none	60	13 min	–	–	8000	Dynamic	8	–
C5	C5.a	COOH	10x	60	1 min	–	–	8000	Dynamic	5	–
	C5.b	COOH	10x	60	30 sec	–	–	1000	Static	4	–
C6	C6.a	amine	none	83	1 min	–	–	1000	Static	4	–
Processing Run #2											
C6	C6.b	amine	none	120	1 min	–	–	8000	Dynamic	1	–
	C6.c	amine	none	168	8 min	15	12000	8000	Dynamic	10	–
C7	C7.a	pristine	10x	138	1 min	–	–	8000	Dynamic	1	1 hr anneal, 390 °C/H ₂
	C7.b	pristine	10x	138	3 min	–	–	8000	Dynamic	1	–
C8	C8.a	COOH	100x	148	1 min	–	–	8000	Dynamic	2	1 hr anneal, 390 °C/H ₂
	C8.b	COOH	100x	148	2 min	–	–	8000	Dynamic	2	–
	C8.c	COOH	100x	148	3 min	15	12000	8000	Dynamic	10	–
C9	C9.a	COOH	none	136	3 min	15	12000	8000	Dynamic	5	–
Processing Run #3											
C10	C10.a	amine	none	242	3 min	10	5000	8000	Dynamic	10	–
	C10.b	amine	none	272	3 min	10	10000	8000	Dynamic	10	–
	C10.c	amine	none	120	2 min	10	10000	8000	Dynamic	10	–
	C10.d	amine	none	360	2 min	10	10000	8000	Dynamic	10	–
C11	C11.a	pristine	none	246	3 min	10	5000	8000	Dynamic	10	–
	C11.b	pristine	none	274	3 min	10	10000	8000	Dynamic	10	–
C12	C12.a	COOH	none	247	3 min	10	5000	8000	Dynamic	10	–
	C12.b	COOH	none	276	3 min	10	10000	8000	Dynamic	10	–

Immediately after these steps, the solutions were spin-coated onto silicon dioxide/n⁺⁺ silicon substrates using a Laurell Spin Processor (Model WS-400B-6NPP/LITE). Some samples were statically spun, by placing drops of the solution on the substrate before running the spin processor, usually at 1000 RPM. Other samples were dynamically spun, in which drops of the solution were deposited on the substrate after the spin processor reached full speed, usually 8000 RPM. Samples were spun with different numbers of drops of solution. After spinning, all samples were rinsed and soaked in isopropanol (IPA) and then dried off with nitrogen. In the third processing run, the pristine samples were also rinsed and soaked in methanol following the IPA soak to remove any remaining surfactant. Two samples (7a and 8a) were annealed at 390 °C in H₂ gas for one hour, prior to metallization. Unfortunately, the yields on samples 7 and 8 were too low to reach any conclusions. Please refer to table 1 for more specifics on how all samples from the three sample sets were processed.

Various sample cleaning methods were evaluated because the resulting CNT films and substrates were noticeably covered with residue after solution deposition. One method was rinsing (while spinning) or soaking the sample with IPA, and perhaps water, for varying lengths of time, then drying it off with nitrogen. Samples created from the pristine CNT solution were rinsed and soaked in demineralized water for an hour in order to remove the surfactant and Nanospense, then dried with nitrogen. A third method, which was found to be the most effective, involved soaking the samples for 90 s in each of the following solvents: first toluene, then acetone, then IPA, and then demineralized water, with a nitrogen dry after each soak.

Further experiments were completed to attain more reproducible, uniform CNT films with desired characteristics. For samples C14.a and b, shown in figure 13, instead of using an ultrasonic bath, the solutions were sonicated with a Sonics VibraCell VCX130 probe sonicator at a frequency of 20 kHz. Having a probe inserted directly into 1 to 4 mL of CNT solution more effectively disperses the tubes than a bath sonicator; therefore, significantly shorter sonication times can be used, ranging from 4 to 30 min. (The amplitude of the probe sonicator was set to 20% or 50% with a 50% duty cycle.)

In other experiments, the spin-processor speeds were varied to determine how the tube density changed with spin speed, if at all. Dynamic spins at speeds of 500, 1000, 3000, and 8000 RPM were used to make CNT films. Static spins were compared to dynamic spins at different speeds using pristine CNT solutions and COOH-functionalized CNT solutions to see if preferential alignment of tubes was attainable. The number of drops of solution deposited during dynamic spins was varied to see if this impacted tube density. Another attempt at controlling tube density involved the comparison of a sample created from one static spin; a sample created from three consecutive static spins, allowing the sample to dry between spins; and a sample created from three consecutive static spins, placing the sample on a hot plate at 65 °C for 30 s between spins.

The drop-casting of CNTs onto substrates was also investigated. Initially, an eye dropper was used to drop-cast the CNT solutions. Ultimately, an Eppendorf micropipette was used to deposit very small volumes of solution onto selected areas of the substrate, with volumes ranging from 1 to 10 μL . A related test involved dip-coating substrates in a CNT solution, in which substrates were dipped into a vial of solution for varying durations of time. The vial was placed in a beaker with a watch glass on top to avoid excessive evaporation of the solution while immersing the substrate. Each sample was then immediately dried off with nitrogen upon removal from the CNT solution. This test was done to see if the density of tubes could be controlled with soak time and to see if the thick ring of tubes that results from drop-casting could be avoided.

To characterize the solution deposited CNTs, the samples were imaged on a Hitachi S-4500 Scanning Electron Microscope (SEM). Observations were made on tube distribution and agglomeration, tube density, tube alignment, tube length, and sample contamination. All samples from the first three processing runs were then ready for the device fabrication and processing stage.

2.2 Device Fabrication and Processing

The CNT films created in the first three processing runs were processed to create back-gated CNTFETs with silicon as the gate, gold electrodes as the source and drain, and CNTs as the channel. Figure 1 illustrates each step of this standard microprocessing procedure. Steps (a) and (b) of figure 1 represent the solution deposition process described in section 2.1. Next, all samples were spin-coated with lift-off resist (LOR7B) for 45 s at 4000 RPM using a Headway manual photoresist spinner, and then baked for 5 min at 170 $^{\circ}\text{C}$. Then the samples were spin-coated with positive photoresist (AZ 5214) for 30 s at 4000 RPM and baked for 1 min at 110 $^{\circ}\text{C}$, shown in step (c).

After spinning resist, the device mask was aligned to each sample with hard contact, and then exposed to ultraviolet (UV) light for 2.2 s, using a Karl Suss MA6/BA6 Mask Aligner (shown in steps (d) and (e)). Samples were developed for approximately 42 s in a 1:1 solution of positive photoresist developer (AZ 312MIF) and deionized (DI) water. Then they were rinsed with running DI water for about 30 s, with the result shown in step (f).

Following the developing step, an adhesion layer of 25 \AA chromium and a 2500 \AA layer of gold were electron-beam evaporated onto the samples using a CHA Electron Beam Evaporator, shown in step (g), followed by lift-off. Samples were placed in a dish of Remover PG on a hot plate set at 70 $^{\circ}\text{C}$ and gently agitated with tweezers to induce lift-off. After most of the gold lifted off, each sample was moved to a second bath of Remover PG for approximately 10 min. Then, each sample was soaked in IPA for 5 min, rinsed under running DI water for 1 min, and then dried with nitrogen. This process resulted in devices ready to test for transistor properties, shown in step (i).

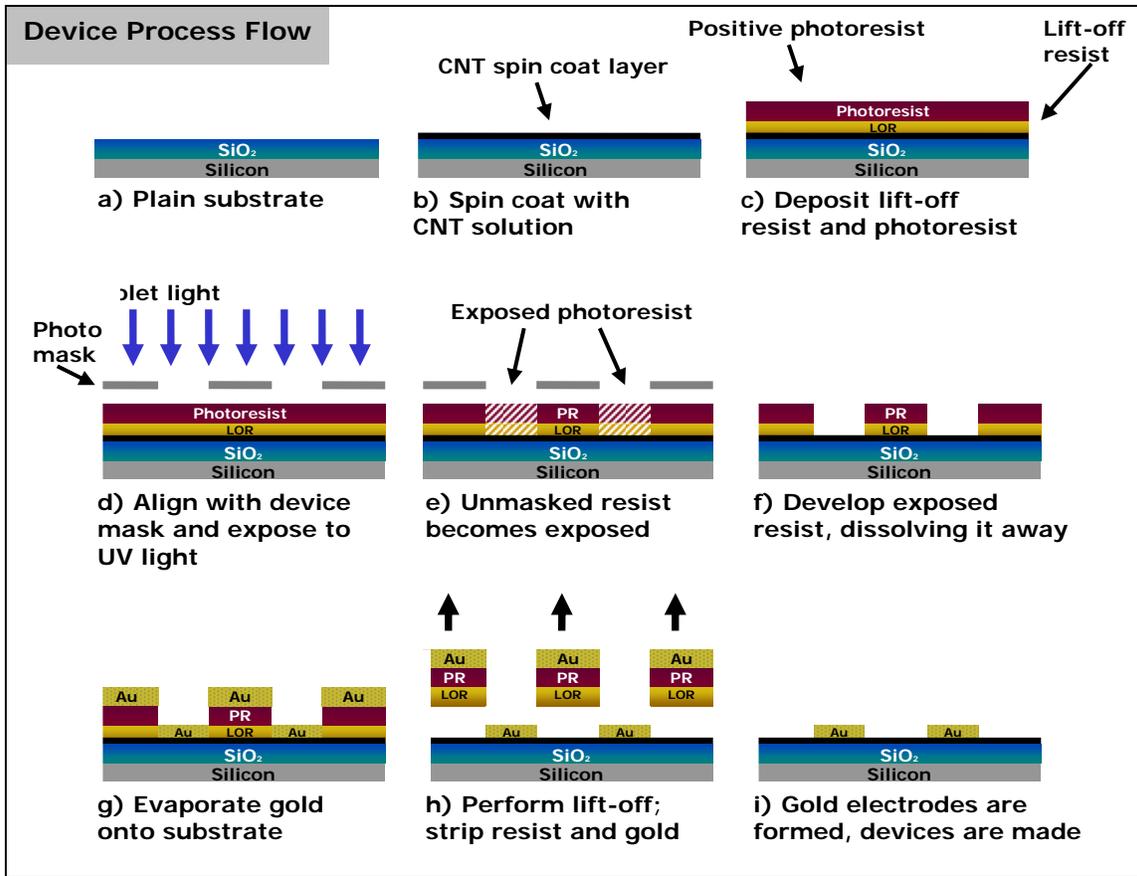


Figure 1. Standard microprocessing techniques used to fabricate CNTFET devices.

Following fabrication, samples were characterized using the SEM to observe CNT distribution in the gaps between device electrodes. Two samples, C4.b and C5.a, underwent post-processing experiments such as a standard 10-min piranha cleaning and a plasma ash, respectively, because the CNT coverage was overly dense. The tubes between the electrodes were protected during the 3-min plasma ash with patterned photoresist, while the uncovered tubes were removed. The photoresist was cleaned off with acetone, leaving behind devices with patterned CNT coverage. After these treatments, samples C4.b and C5.a were observed in the SEM to determine the effects on tube density and dispersion.

2.3 Electrical Testing

Using a Keithley 4200 Semiconductor Characterization System, each sample's CNTFET devices were tested for transistor behavior. Each sample was measured on a probe station's conductive vacuum chuck, with the chuck making contact with the gate as they are back-gated devices. In the first two processing runs, typically 96 devices per sample were produced, depending on how many device sets could be aligned to fit on the substrate. In the third processing run, up to 44

devices per sample were produced. The source/drain bias voltage was set to 0.25 V, the gate voltage was swept from -15 V to 15 V, and current-voltage (I-V) curves were gathered from these tests to observe any metallic and semiconducting characteristics from the tubes.

Some samples were annealed to improve the contact resistance of the devices. Samples C3.c and C4.a were annealed at 515 °C in H_2 gas for one hour. Samples C6.b, C6.c and C9.a were annealed at 250 °C in argon gas for one hour. These anneals were conducted in the CVD growth furnace.

3. Results and Discussion

Each CNTFET device on each sample was measured for transistor behavior to evaluate the solution deposition conditions for all the samples. The qualitative observations on the electrical properties of the devices are shown in table 2 and also include any post-processing treatments on certain samples and their subsequent electrical properties. The most successful samples were evaluated as having a high percentage of semiconducting devices and high on/off ratios. A generalized observation about tube density from electrical testing data is that higher tube density samples produce mostly metallic devices, moderate tube density samples produce semiconducting and semi-metallic devices, and low tube density samples produce very few devices. These conclusions were arrived at by correlating the SEM micrographs with the electrical testing results.

Observations on CNT films and related samples processed in the latter half of the project were based solely on SEM micrographs because they were not made into CNTFET devices. To compare tube densities between samples, SEM images were taken at similar magnifications on each sample. Another key characteristic to look for was overall uniformity of the tube density and tube distribution across the sample. Average tube lengths were estimated from SEM images.

Table 2. Qualitative results from measurements on the Keithley 4200 Semiconductor Characterization System.

Processing Run #1					
Solution	Sample	Functionalization	Electrical Properties	Post-Processing	Change in Electrical Properties?
C3	C3.c	pristine	low current, noisy, ~semi-metal	1 h anneal at 515 °C/H ₂	higher current, still a bit noisy, ~semi-metal
C4	C4.a	COOH	high current, noisy, metallic/strange	1 h anneal at 515 °C/H ₂	similar strange properties, leaky, reaches compliance
	C4.b	COOH	high current, noisy, metallic/strange	10 min piranha clean	similar strange properties, leaky, reaches compliance
C5	C5.a	COOH	high current, noisy, metallic/strange	Plasma ash tubes outside active region	metallic, extremely high current, ~60 μA max
	C5.b	COOH	high current, noisy, metallic/strange	–	–
C6	C6.a	amine	low current, noisy, ~semi-metal	–	–
Processing Run #2					
C6	C6.b	amine	low current, noisy, ~semi-metal	1 h anneal at 250 °C/Ar	higher current in 100 s of nA, less noisy, more semi
	C6.c	amine	avg current, low noise, semiconducting	1 h anneal at 250 °C/Ar	very high current: μA range, a bit noisy, some “dead”?
C7	C7.a	pristine	very few devices found	–	–
	C7.b	pristine	very few devices found	–	–
C8	C8.a	COOH	very few devices found	–	–
	C8.b	COOH	NO devices found	–	–
	C8.c	COOH	very few devices found	–	–
C9	C9.a	COOH	a few devices found, 1 good one	1 h anneal at 250 °C/Ar	not much change observed in the few devices
Processing Run #3					
C10	C10.a	amine	many devices, high current, semi, thin curve	–	–
	C10.b	amine	low current, noisy, ~semiconducting	–	–
	C10.c	amine	higher current, ~semi-metal/semi, noisy	–	–
	C10.d	amine	mostly low current, noisy, ~semi/semi-metal	–	–
C11	C11.a	pristine	very few devices, if found, very low current, noisy	–	–
	C11.b	pristine	very few devices, if found, very low current, noisy	–	–
C12	C12.a	COOH	high current, noisy, metallic/strange, leaky	–	–
	C12.b	COOH	high current, noisy, metallic/strange, leaky	–	–

3.1 Comparison of Functionalization of CNTs

Based on initial data collected from the three processing runs, the aminopyrene non-covalently functionalized CNTs produced the most favorable results for CNTFET devices. Out of the seven amine samples processed, all samples showed evidence of semiconducting behavior in the CNTs. While NanoLab, Inc., the company from which the original CNT solutions were purchased, specified that the COOH-functionalized tubes were more soluble, only one sample, C9.a, out of the 10 COOH samples showed any transistor characteristics. This observation may be due to certain experimental conditions, such as over-dilution or excessive solution deposition, preventing actual analyzable data from being gathered. The 100× dilution to the C8 COOH-functionalized solution in the second processing run resulted in very sparse surfaces, as pictured in figure 2(a), and few devices. The non-diluted COOH-functionalized tube solutions mainly resulted in samples so dense with tubes (see figure 2b) that the entire surface was conductive, interfering with I-V curve acquisition. Further optimization of the COOH-functionalized tube processing will be discussed later, to determine if a better yield of devices could result from COOH-functionalized CNTs.

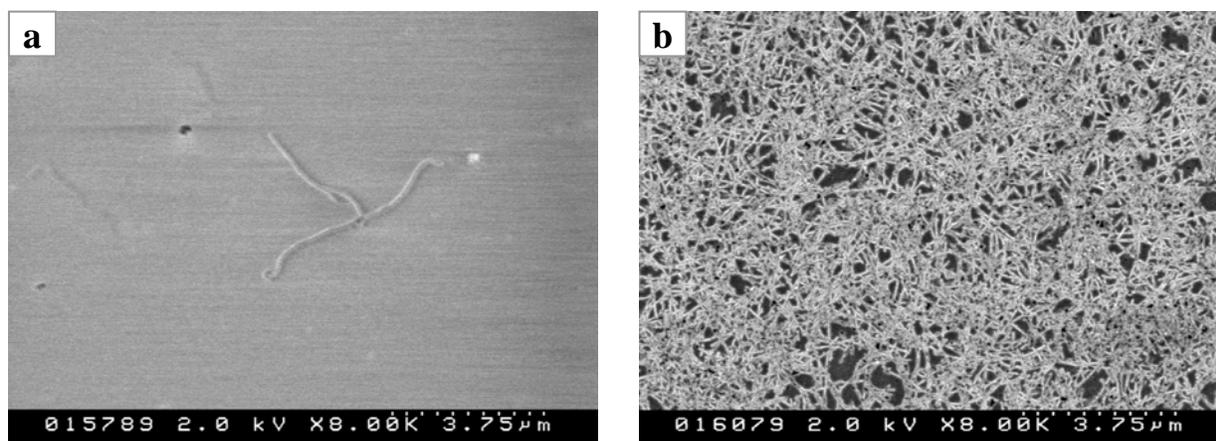


Figure 2. Examples of the deposition issues encountered with COOH-functionalized CNT solutions: (a) a 100× diluted solution with centrifugation resulted in very few tubes and not many CNTFET devices and (b) a non-diluted solution with centrifugation resulted in a thick web of CNTs causing the entire surface to be conductive, overwhelming any transistor behavior. (C8.c, C12.a).

The pristine samples did not produce many good devices, but a total of only five samples were fabricated in these runs. The first pristine sample, C3.c, had many devices with semiconducting behavior, but the four following samples produced very few devices due to sparse tube surface densities, as pictured in figure 3. The scarcity of tubes may be due to the methanol rinse and soak introduced for the second and third processing runs, as recommended by a representative of NanoLab, Inc., to remove any remaining surfactant. We were concerned that the methanol may have caused the tubes to resolubilize and wash off the substrate. In later experiments, newly spun pristine samples were characterized with the SEM before and after soaking to determine whether or not the tubes were being washed off. It was found that tubes were not washed off by this cleaning process.



Figure 3. Example of the low tube density for most pristine samples, resulting in very few working devices. (C11.a).

3.2 Comparison of Centrifugation of CNT Solutions

Centrifugation of the solutions prior to spinning was introduced in the second processing run after reading about the importance of this step for removing bundles of tubes in multiple papers (e.g., Nouchi et al. [5]). After centrifuging small amounts of the solutions, it was noted that the pristine solutions appeared very clear, while the amine solutions appeared more tinted and the COOH solutions appeared the most tinted. This tinting could indicate that COOH-functionalized tubes are the most soluble, with more tubes remaining in solution even after undergoing centrifugation, while aminopyrene non-covalently functionalized tubes are less soluble, and pristine tubes are the least soluble. Overall, it was observed that centrifugation reduces the concentration of tubes in solution, and consequently reduces the tube density on the surface.

For the COOH-functionalized tubes, the decreased density is somewhat apparent, when comparing the non-centrifuged sample shown in figure 4(a) with the centrifuged sample shown in figure 4(b). Despite this difference, neither sample produced semiconducting CNT behavior in its devices, indicating that other factors influence the results. We believe that the COOH samples still had too many tubes to exhibit semiconducting behavior because of the dominant metallic tube contributions.

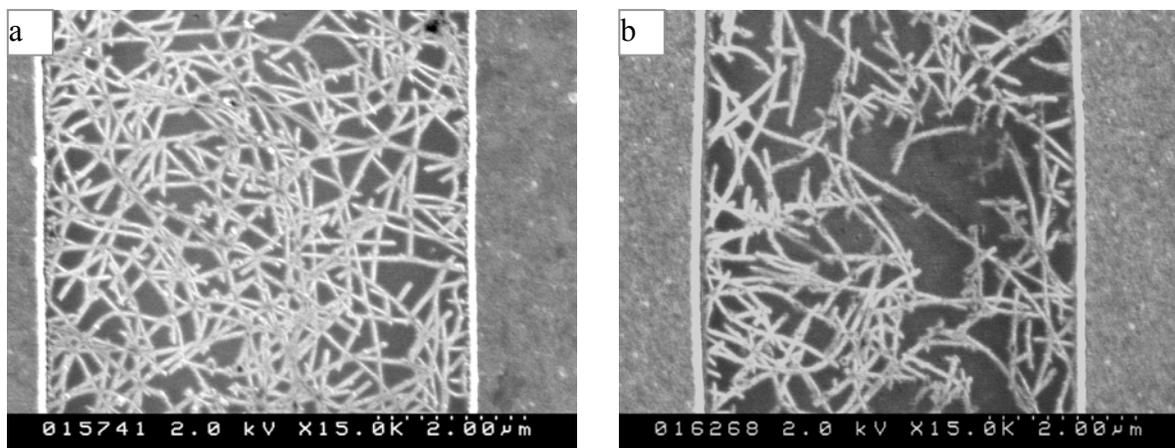


Figure 4. A comparison of the effects of centrifugation on tube distribution with SEM images. (a) (C4.b) and (b) (C12.b) were spun-cast with similar conditions and non-diluted solutions of COOH-functionalized CNTs. The sample in (b) underwent centrifugation for 10 min at 10,000 RPM, causing the overall concentration of the solution to decrease and reducing the surface density of CNTs deposited. (C4.b, C12.b).

Centrifugation of the aminopyrene non-covalently functionalized tubes caused the tubes to be less agglomerated on the surface, shown in figure 5(c), than the non-centrifuged samples, shown in figure 5(a) and figure 5(b). The tubes in sample (a) were statically spun, resulting in a significantly agglomerated CNT film. The tubes in sample (b) were dynamically spun, resulting in better dispersion. However, the tubes in sample (c) were the least agglomerated because of the centrifugation step and appear more uniformly distributed. All of these samples produced semiconducting devices, but it was the centrifuged sample (c) that had higher on/off ratios for its CNTFETs. Centrifugation seems to have a positive influence on the overall tube distribution of the aminopyrene samples. The pristine samples had too few tubes to make any observations on the effects of centrifugation.

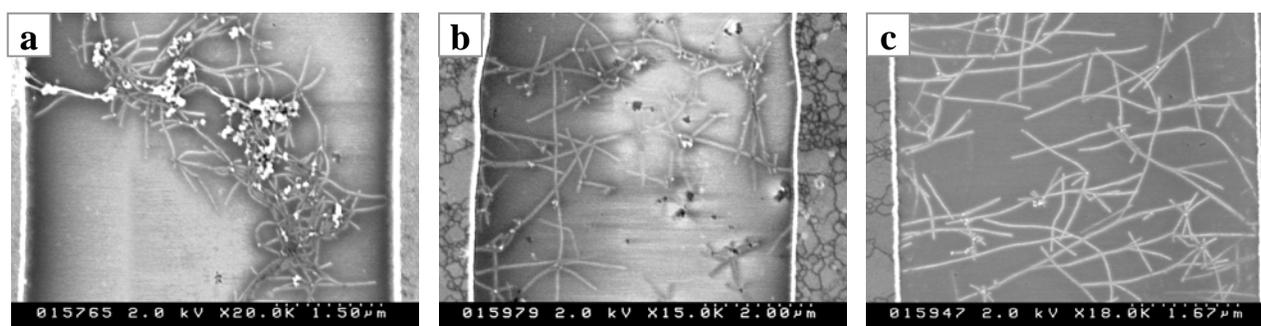


Figure 5. An SEM comparison of the effects of centrifugation on tube distribution with SEM images. All samples were spin-cast with non-diluted solutions of aminopyrene non-covalently functionalized CNTs. The sample in (a) was statically spun with no centrifugation, the sample in (b) was dynamically spun with no centrifugation, and the sample in (c) was dynamically spun after centrifugation for 15 min at 12,000 RPM, causing the overall concentration of the solution to decrease and reducing the surface density of CNTs deposited. (C6.a, C6.b, C6.c).

Variations on the centrifuge RPM were made in the third processing run with the time set to 10 min and the RPM set to either 5000 RPM or 10,000 RPM. Figure 6 compares a 5000 RPM sample to a 10,000 RPM sample. For the COOH samples, it appears that the higher the RPM, the less dense the coverage. This is not surprising as the higher RPM should pull more of the CNTs out of solution and into the pellet at the bottom of the centrifuge tube. However, yet again, neither of these two samples produced the main goal of semiconducting CNTFET devices. Therefore, further testing must be done with COOH samples processed into CNTFET devices to determine the best balance of dilution, centrifugation, and other conditions in the solution deposition methods to yield an appropriate tube density.

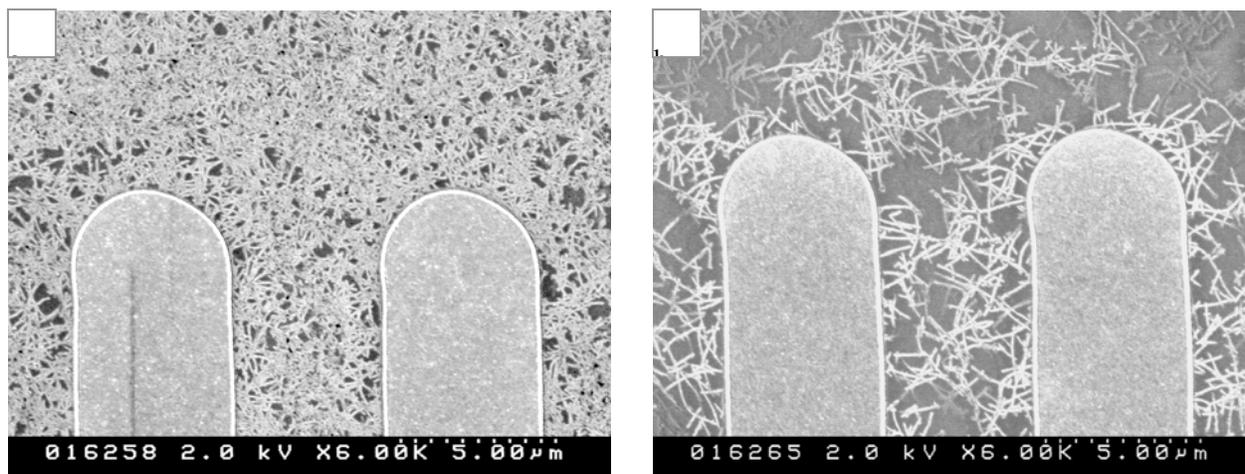


Figure 6. A comparison of the effects of centrifugation RPM. The samples shown in (a) and (b) were spin-cast with similar conditions, both non-diluted solutions of COOH-functionalized CNTs and centrifuged for 10 min. The sample in (a) underwent centrifugation at 5000 RPM, while the sample in (b) underwent centrifugation at 10,000 RPM. (C12.a, C12.b).

For the aminopyrene samples, we also observed that, the higher the centrifuge RPM, the less dense the CNTs are. Figure 7 compares a 5000 RPM sample to a 10,000 RPM sample. The higher centrifugation RPM helps to reduce the overall tube agglomeration on the sample surface. The aminopyrene samples appear better separated than the COOH samples shown in figure 6, and both aminopyrene samples showed evidence of semiconducting CNTs upon electrical testing. While the low-spin aminopyrene sample appears to have more tubes than the high-spin COOH sample, it may have fewer electrically active tubes due to contamination, which may reduce the electrically active tube density into the semiconducting range.

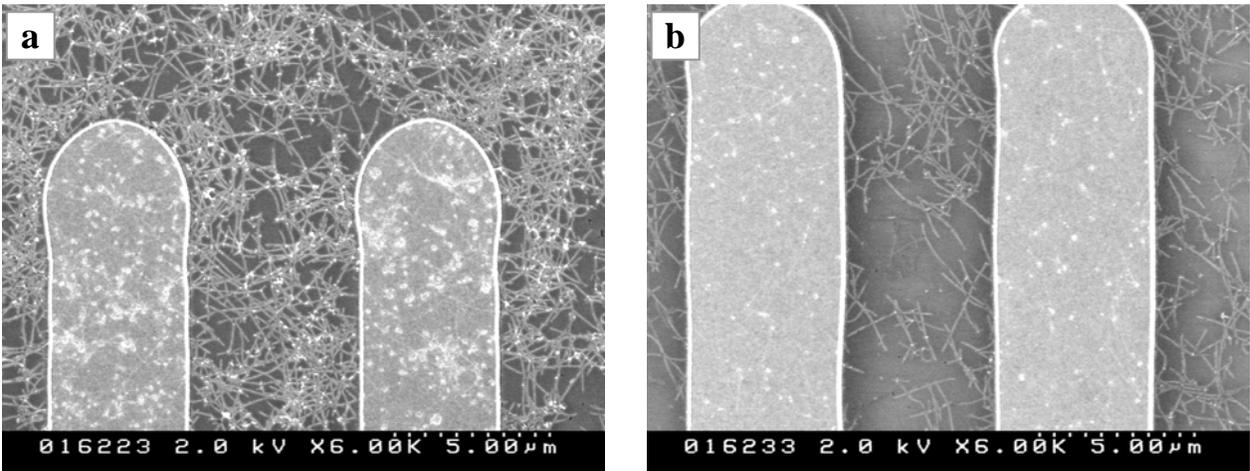


Figure 7. A comparison of the effects of centrifugation RPM. The samples shown in (a) and (b) were spin-cast with similar conditions, both non-diluted solutions of aminopyrene non-covalently functionalized CNTs and centrifuged for 10 min. The sample in (b) underwent centrifugation at 10,000 RPM, while the sample in (a) underwent centrifugation at 5000 RPM. (C10.a, C10.b).

3.3 Comparison of Annealed Samples

Prior to annealing, many samples showed very low source/drain current and were very noisy. The annealing presumably improved the device contact resistance, reducing the noise and increasing the source/drain current of the CNTFETs for the aminopyrene samples and the single annealed pristine sample. The I-V curve in figure 8 shows the initial data acquired before annealing, with a maximum on-current value of 75 nA and a slightly noisy curve. Figures 8 and 9 plot the source and drain currents on the left axis scale and the gate current on the right axis scale. All three currents are monitored in order to have a full accounting of the device current (e.g., so that gate leakage is not mistaken for source-drain current). After annealing the sample, the on-current increased by nearly a factor of 10, but the off-current also increased significantly, as shown in figure 9. Therefore, overall the annealing step seems to help the aminopyrene samples, but sometimes the on/off ratio may be negatively affected. We believe that the annealing increased the number of tubes electrically contacted, some of which were metallic, resulting in the higher off-current. This supports the supposition that not all of the aminopyrene functionalized tubes are electrically active to start with. The annealing did not appear to improve any of the COOH samples, probably because they were too conductive (metallic) to begin with.

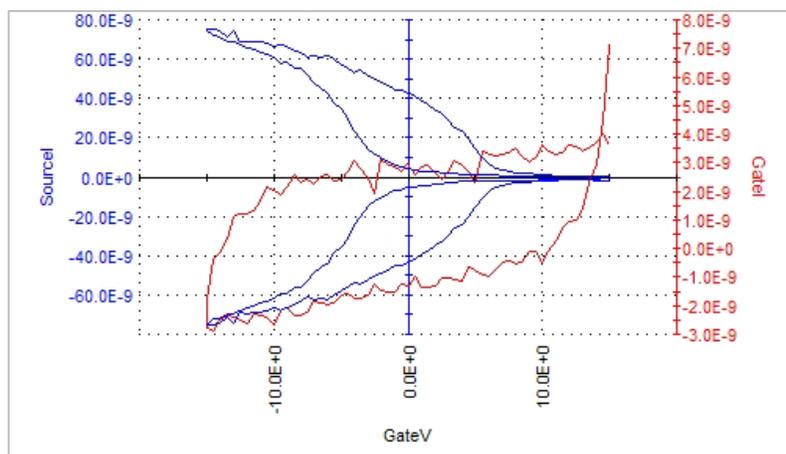


Figure 8. I-V curve of an aminopyrene non-covalently functionalized sample prior to annealing. Source and drain currents are plotted on the left axis scale and the gate current is plotted on the right axis scale. (C6.b).

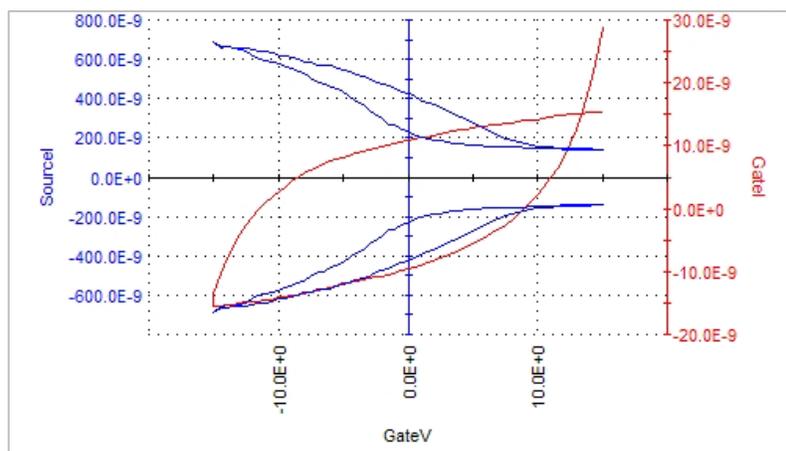


Figure 9. I-V curve of an aminopyrene non-covalently functionalized sample after annealing. (C6.b).

3.4 Raman Spectroscopy Analysis

Micro-Raman spectroscopy mapping was completed using a Renishaw Raman Microscope ($\lambda = 633 \text{ nm}$ at 50% power). Mapping was done on regions between pairs of electrodes on the aminopyrene non-covalently functionalized sample C10.a before and after annealing 1 h at $250 \text{ }^\circ\text{C}$ in air, shown in figures 10 and 11, respectively. The data appeared similar before and after annealing, with the only change being an overall decrease in intensity of the peaks. The cause of this decrease is likely a measurement artifact due to focusing on a slightly different region of the sample and also due to the instrument alignment. The Raman spectra show that the solution deposited samples are similar to a CVD-grown sample, whose spectrum is shown in figure 12 for comparison. All of the Raman spectra show characteristic peaks for CNTs (RBM, D, and G peaks), while the solution processed sample spectra have some additional peaks. The

additional peaks may be evidence of the aminopyrene coating of the CNTs, but this has not been confirmed. If this is the case, the sample annealing did not evaporate the aminopyrene off of the tubes, which is a good sign if it is needed for subsequent functionalization of the tubes for sensing applications.

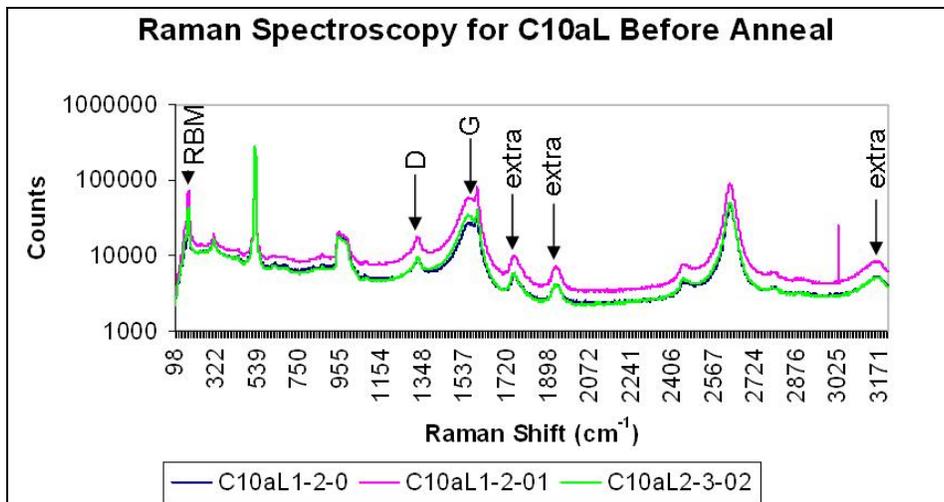


Figure 10. Raman spectra from three locations on sample C10.a prior to annealing, $\lambda = 63 \text{ nm}$.

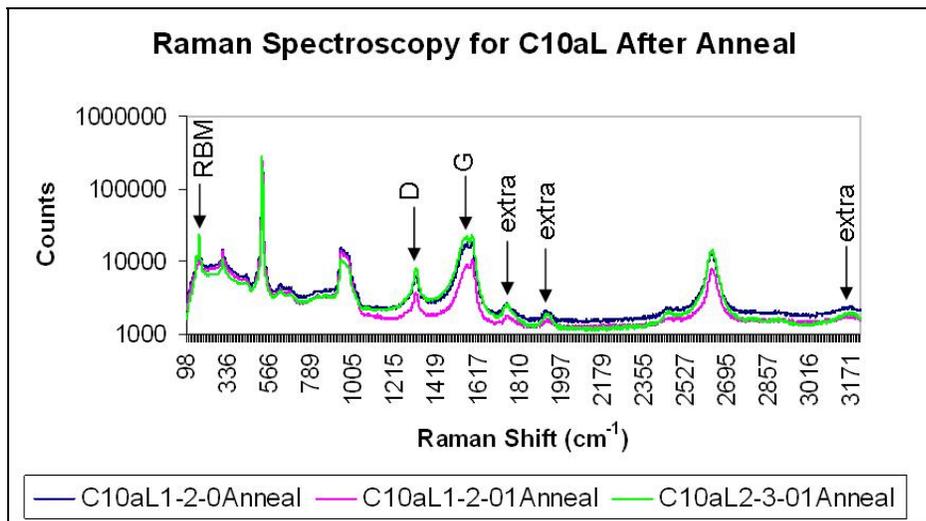


Figure 11. Raman spectra from three locations on sample C10.a after annealing, $\lambda = 633 \text{ nm}$.

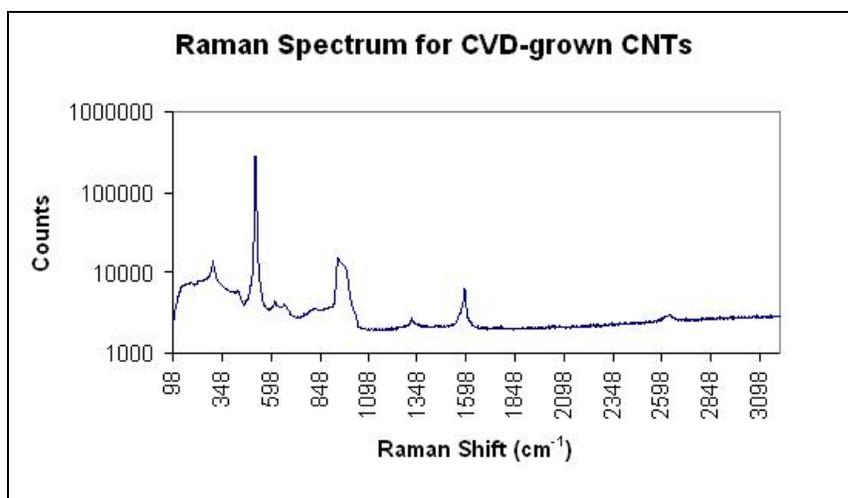


Figure 12. Raman spectra of a CVD grown CNT sample (CNT078b) for comparison, $\lambda = 633$ nm.

3.5 Comparisons of Spin Speed and Drop Casting

For one experiment, two different spin-coat speeds were tested to see which conditions produced a more uniform CNT film. The aminopyrene samples were dynamically spun at 500 and 8000 RPM (figure 13). Both samples appear to have a similar high tube density, which is fairly consistent across both sample surfaces. This is initially somewhat surprising, but spin speed is usually used to affect the thickness of a deposited film. If different thicknesses of the CNT solutions were deposited, different amounts of CNTs should result. However, the CNT solutions appear to be entirely spun off in the process, so that the tube density may be a function of the time the solution is in contact with the substrate, but not particularly dependent upon spin rate. Similarly, dip coating tubes onto substrates did not have a strong correlation of tube density with the amount of time the substrates were in the CNT solution. It may be that dip coating is essentially dominated by the effective drop casting that occurs as the solution dries on the substrate when it is removed from the solution.

Drop-casting techniques did not distribute the CNTs as well as spin-coating. The advantage of this method is that the CNTs could be deposited on a selected area on the sample. However, the drying of the drops leaves behind a visible ring of tubes around the circumference of the drop. While the time spent soaking in the CNT solutions or spin speeds did not appear to control the tube density well, the tube density could be increased using repeated CNT depositions.

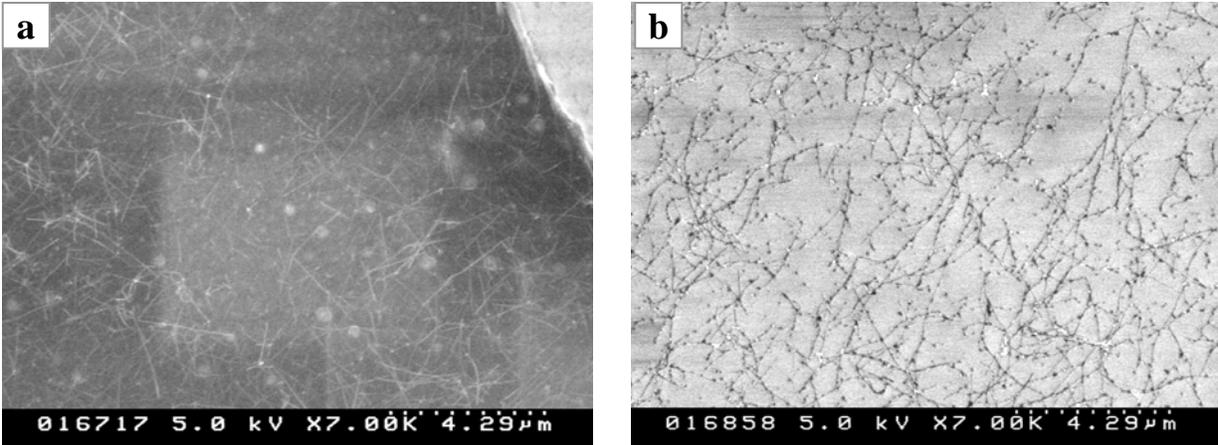


Figure 13. A comparison of the effects of dynamic spin speed. The samples shown in (a) and (b) were spin-cast with similar conditions, both non-diluted solutions of aminopyrene non-covalently functionalized CNTs and centrifuged for 10 min. The sample in (a) was spun at 500 RPM, while the sample in (b) was spun at 8000 RPM. (C14.a, C14.b).

4. Summary and Conclusions

We have developed a solution-based process for depositing CNTs onto substrates for processing into FETs. This process, while amenable to using tubes of different functionalizations (e.g., COOH, aminopyrene, and pristine tubes), requires optimization for each type of tube. To this point, the aminopyrene non-covalently functionalized CNTs have produced the most reproducible, predictable CNTFET devices. These samples have had the highest yield in semiconducting devices. However, different types of tube functionalization may be useful for facilitating further functionalization of the CNTFETs in order to produce CNTFET-based chemical sensors. The deposition of CNTs from solution will provide additional flexibility for chemically modifying the tubes for sensing various analytes.

There are many variables that still need to be optimized, particularly for the COOH and pristine solutions. The CNT solution concentration and centrifugation parameters are factors that have a significant effect on the resultant tube densities. Other parameters such as spin speed or dynamic versus static spinning do not appear to have a strong effect on the resulting CNT films. While there are literature reports that a dynamic spin can produce preferable alignment of CNTs (3), tube alignment has not yet been achieved here. The CNT tube densities have been found to greatly affect the resulting FET properties. Too few tubes, and there is poor device yield. Too many tubes and the devices can be dominated by the metallic characteristics of some of the tubes. Large tube densities also results in gate leakage if the tubes cover the entire surface of the sample. Post-metallization annealing improves contact resistance and increases the device current for the aminopyrene samples.

Future work will focus on optimizing the existing methods to produce reproducible, predictable CNTFET devices for various applications. Newly fabricated samples will undergo chemical sensing tests with gases such as ammonia. These sensing results will be compared with similar tests done on CVD-grown CNTFET devices.

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List of Symbols, Abbreviations, and Acronyms

CNTs	carbon nanotubes
CNTFETs	carbon nanotube field-effect transistors
CVD	chemical vapor deposition
DI	deionized
IPA	isopropanol
I-V	current-voltage
SEM	Scanning Electron Microscope
SWNTs	Single-walled carbon nanotubes
TFTs	thin film transistors
TARDEC	Tank and Automotive Research, Development and Engineering Center
UV	ultraviolet

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