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Percolation in networks of aligned SWNTs formed with laminar flow deposition

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Abstract Macroscopic networks of highly aligned SWNTs have been fabricated at room temperature by laminar flow deposition from aqueous suspensions. This deposition method allows the growth of a macroscopic two dimensional SWNT network through successive deposition cycles. AFM image analysis showed that each deposition cycle puts down a reproducible density of SWNTs, with the final density being directly proportional to the number of deposition cycles for a given solution. The macroscopic electronic behavior of these networks was characterized by DC conductance measurements taken after each deposition cycle. This showed that these networks could be described by two dimensional percolation models throughout the growth process.

Introduction

Macroscopic thin-films with optical transparency and electrical conductivity find many applications in contemporary and emerging technologies, such as displays of various kinds [1], solar cells [2], electro-chromic devices [3], and heatable glass [4]. Further, single-walled carbon nanotube (SWNT) networks have high conductivity, carrier mobility, and exhibit optical transparency in the visible range [5]. These properties present the possibility of creation of enhanced electronic device structures like diodes [6], field-active optical modulators [5], chemical sensors [7], thin-film transistors [8], field-emission transistors [9], and transparent conductive coatings [5]. Two dimensional networks of SWNTs have shown great promise in all of these applications, yet the lack of methods for reproducible formation of ordered thin-films of SWNTs remains a major impediment to their widespread use in electronic device structures.

Two dimensional networks of electrically continuous SWNTs are also potential alternatives to indium tin oxide, which has limitations due to its lack of flexibility, high cost, environmental concerns regarding indium mining, and requirement for high-temperature vacuum deposition [10]. SWNT networks, in contrast, have high mechanical flexibility and environmental resistance [11], and can be fabricated using various room-temperature techniques, including printing [9, 12], or spraying technologies [13].

This group's laminar flow deposition (LFD) method is a significant step towards the realization of many applications of SWNTs, as it allows formation of a network of any desired density; variations in an SWNT suspension's concentration and/or the number of deposition cycles provide great control in the thin-film growth process. This is of great importance because if the density of a two dimensional SWNT network is strictly controlled, the network can be tailored to behave as either a thin-film semiconductor or metal; low-density networks behave as semiconductors, while high-density networks exhibit metallic conduction [12].

This manuscript presents data regarding the development of a new deposition technique for the formation of networks of SWNTs with enhanced control over density and orientation. A strong correlation between the density of SWNTs on the surface and the observed macroscopic electrical resistance will be demonstrated. Although a great degree of alignment was observed, the fact that a

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significant number of errant (non-aligned) SWNTs existed in deposits caused the observation of macroscopic electrical conduction at lower loadings of SWNTs than would be required for perfectly aligned nanotubes. Therefore, these non-aligned SWNTs are largely responsible for the macroscopic conduction of these networks at sub-monolayer coverage. Consequently, the evolution of the SWNT network's resistance with each deposition cycle can be approximated using percolation theory, as applied to a random two dimensional network of conducting sticks eventhough the majority of SWNTs are aligned.

Experimental section

Substrate preparation

A dual-filament thermal evaporator (Thermionics) with tungsten boats was used to deposit Ti (99.995% pure, 1/8″ in diameter pellet, Kurt J. Lesker Company) electrodes on a 4-inch Si wafer (P-Type, 3000A thermal Oxide, Montco Silicon Technologies Inc.). The deposition occurred under high-vacuum at $P < 1 \times 10^{-6}$ torr. A homemade stainless steel stencil was placed between the deposition source and Si wafer to form the patterned electrode arrays. These electrodes were a square pattern of 2 mm diameter Ti dots with a spacing of 1 cm. The thickness of the Ti electrodes was verified to be 500 nm with AFM imaging. The Si wafer was cut into fragments of 2 cm × 1 cm, with each fragment having two Ti electrodes for conductivity measurements. The fragments were then cleaned with a snow-jet (compressed CO_2), and coated with silane. For the silanization process, 100 µl of 3-amino-propyl-triethoxy-silane (99%, Aldrich) was added to 20 mL ethanol (99.5%, absolute 200 proof, ACROS). The Si wafer fragments were soaked in the silane solution for 45 min. Finally, the silane-coated Si wafer fragments were cleaned with ethanol, water, and a snow-jet (in that order).

SWNT suspension preparation

About 10 mg of unmodified SWNT soot (AP-grade, CarboLex Inc.) was added to 10 mL of 1% (w/w) sodium dodecyl sulfate (SDS, J. T. Baker) solution. Then, the suspension was sonicated with a probe sonicator (Model 500, Fisher) for 30 min at either 6 or 12 W sonication power. Sonication has been previously demonstrated to de-bundle SWNTs in suspensions [14]. Three centrifugation/decantation (GS-15R, Beckman) cycles at 18,000 rcf, lasting 30 min each, were then performed to remove impurities (catalyst metal nanoparticles, amorphous carbon, and remaining SWNT bundles). After each centrifugation, 80% of the supernatant was collected and readied for the next centrifugation cycle. This processing method has proven effective in removing bundles of SWNTs, catalyst nanoparticles, and amorphous carbon, leaving long-unbundled SWNTs in suspension [15]. AFM analysis of the numerous deposits used in this study indicated that the average SWNT length, $l = 0.8$ µm.

SWNT network deposition

Enough clean SWNT suspension was added to the prepared substrate to create a thin layer of the suspension on the fragment surface. Nitrogen flow ($P = 60$ psi) was then applied at an angle of $\sim 30°$ to align the SWNTs in the suspension and dry the solvent (Fig. 1). Then, the substrate was washed with copious nanopure water to remove any remaining SDS residue. Finally, the surface was dried under flowing nitrogen. The above process is defined as

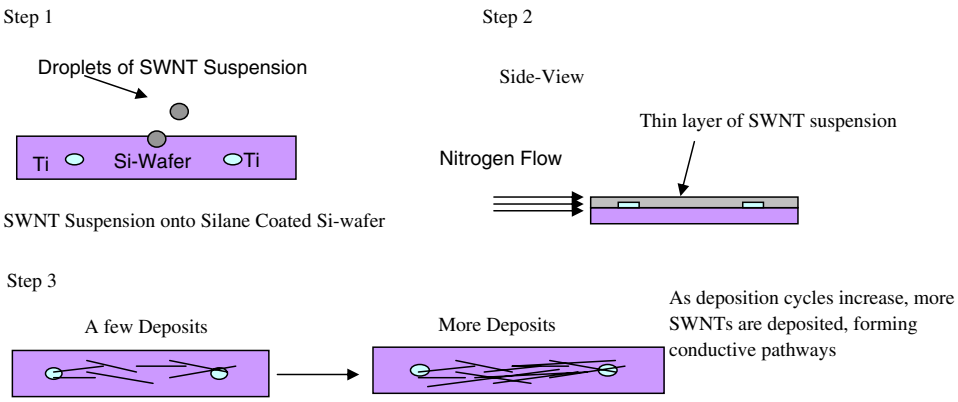

Fig. 1 Flow chart of laminar flow deposition (LFD) method used to fabricate aligned SWNT networks. Step 1: SWNT suspension was drop-cast on a Si wafer substrate (coated with Ti electrodes and silane in a previous step); Step 2: Directional nitrogen flow was to evaporate solvent and align SWNTs in a thin layer of the suspension; and Step 3: Repeated deposition cycles were used to increase the network density

one deposition cycle. For the work presented herein, the nanotube orientation was parallel to the span between the two Ti electrodes on the substrate.

Characterization methods

The morphology of the SWNT networks was characterized by intermittent contact mode atomic force microscopy (AFM, Molecular Imaging, PicoPlus). Samples were imaged with AFM without modification. A semiconductor characterization system (Keithley, 4200SCS) and probe station (Signatone, S-1160A) were used for macroscopic electrical measurements.

Results and discussion

Strict density control for SWNT network formation through LFD

The density of SWNTs deposited in each cycle can be determined by performing a deposition cycle, followed by AFM analysis of several areas of the deposit to count the number of SWNTs deposited per unit area. In order to investigate the effect of suspension preparation on reproducibility of the deposition process, two solutions were prepared: for one solution 6 W sonication power was used to disperse the SWNTs, while for the second solution, 12 W was used. At either sonication power, probe sonication has proved to be an effective way to form stable aqueous SWNT suspensions of individual SWNTs [16].

The initial concentration of SWNTs in each suspension was verified with UV-vis spectroscopy prior to deposition (Fig. 2). For the first data presented, a suspension with a concentration of 1 mg/mL SWNT soot was sonicated at 6 W for 30 min, followed by three centrifugation/decantation cycles. The final concentration of this suspension was determined to be 0.006 mg/mL from analysis of UV-vis spectroscopy calibration curves. Deposits formed from this suspension indicated that the density of highly aligned SWNTs on the surface increased at a rate of 0.37 SWNTs/μm^2 (Fig. 3). This deposition rate was determined to be constant over numerous deposition cycles.

A second suspension, with the same starting concentration as the previous suspension, was sonicated at 12 W for 30 min. This higher sonication power resulted in a more concentrated SWNT suspension. The concentration of this suspension was determined to be 0.02 mg/mL. The greater concentration of the deposition solution resulted in a greater deposition rate for SWNTs on the surface; 0.74 SWNTs/μm^2 for each deposition cycle, which is twice high as the rate obtained from a sonication power of 6 W.

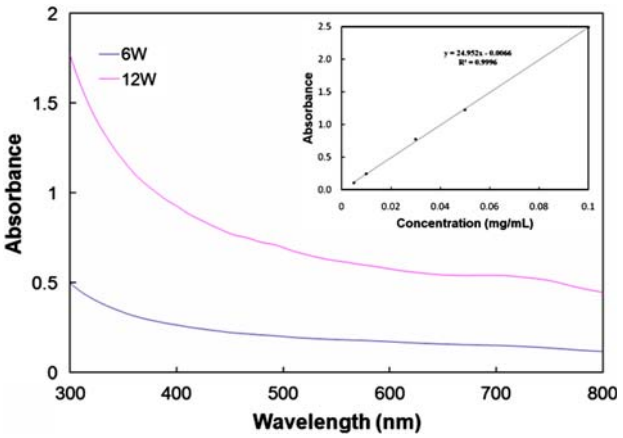

Fig. 2 UV-vis spectra of the two SWNT suspensions used. Even-though the same starting concentration was used (1 mg/mL), increasing the sonication power used to disperse the SWNTs resulted in a significantly higher concentration of dispersed SWNTs. Concentrations of the suspensions after centrifugation were determined to be 0.006 mg/mL (6 W) and 0.02 mg/mL (12 W), from a calibration curve (inset) obtained for a series of solutions measured at 700 nm

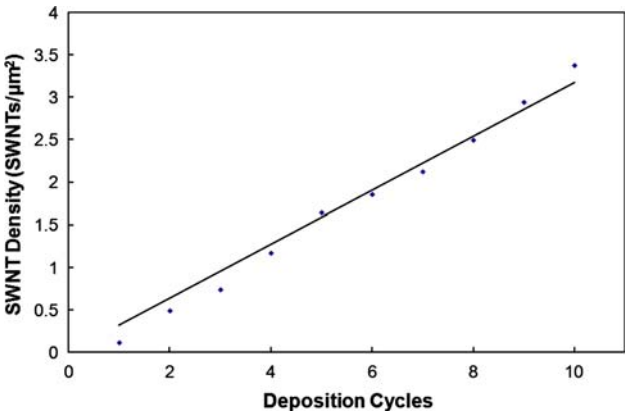

Fig. 3 Density of SWNTs, as measured with AFM, as a function of number of deposition cycles. For SWNTs aligned in one direction, the density of SWNTs increases at a rate of 0.37 SWNT/μm

With repeated deposition cycles, the number of SWNTs on the surface was observed to increase in a linear manner until a high coverage of SWNTs was observed (Fig. 4). Therefore, LFD has the potential to allow formation of any desired network density. The sonication power and initial concentration of the SWNT suspension can easily be modified to allow any arbitrary density of SWNTs be deposited per deposition cycle. Therefore, this group's method can produce a two dimensional network of SWNTs with tunable electrical properties.

Application of percolation theory

The LFD method can lead to the formation of a two dimensional SWNT network with controllable density, as

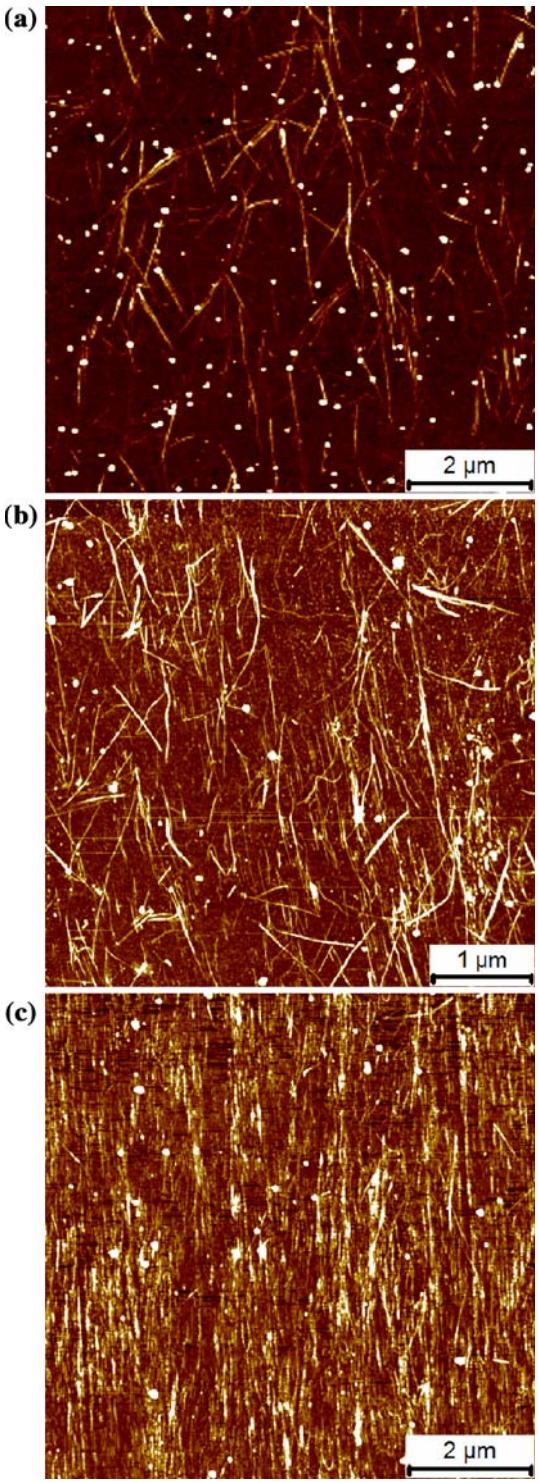

Fig. 4 AFM Images (8 μm × 8 μm) of aligned SWNT deposits formed via LFD method: (**a**) after 5, (**b**) 10, and (**c**) 15 deposition cycles. The average SWNT length and density were determined from analysis of low-density networks

dictated by the concentration of the suspension and number of deposition cycles. Percolation theory is a mathematic model that allows one to estimate when a macroscopic system, composed of micro- or nanoscopic components that define its behavior, will exhibit a particular phenomenon [17, 18]. The application of percolation theory to electrical systems allows one to characterize the flow of electricity through a random network of conductors. Each SWNT corresponds to a conducting stick in percolation theory [19–21]:

$$N_c = \frac{4.236^2}{l^2 * \pi} \quad (1)$$

where, 4.236^2 is a theoretical constant, simulated based on the "randomly aligned conducting sticks" model [19]; l is the average length of the SWNTs; π is the constant that represents the ratio of any circle's circumference to its diameter (as a conducting stick can adopt any angle of rotation); and N_c is the critical density of the SWNT network (above which macroscopic pathways exist).

Equation 1 predicts that $N_c = 8.9$ SWNTs/μm^2 for a random network composed of SWNTs with $l = 0.8$ μm. A network of highly aligned SWNTs is expected to require a greater density of SWNTs to reach N_c, with this density increasing commensurately with the degree of alignment in the layer. However, experimental evidence indicates that the density of aligned networks reaches N_c at a similar number of deposition cycles.

The SWNT suspension sonicated at 12 W was used to form an SWNT network using 20 deposition cycles. Because N (0.74 SWNTs/μm^2 per deposit for this solution) is proportional to the number of deposition cycles, it is predicted that the surface shall begin displaying macroscopic conduction at 12 deposition cycles, as $0.74 \times 12 = 8.9$ and the critical density, N_c of 8.9 SWNTs/μm^2 is met. In fact, experimental results showed that most of the substrates experience an exponential increase in conductance at 12 or 13 depositions (Fig. 5, inset). This confirms there is a predictable increase in the density of SWNTs with the number of deposition cycles.

The fact that percolation theory applies to these networks indicates that although there is a great degree of order, enough randomly deposited SWNTs exist for macroscopic conduction to follow percolation theory as prescribed for random conducting sticks, when confined to two dimensions. Therefore, the alignment effects become more significant when the density reaches a high level. AFM images of low-, intermediate-, and high-density networks (Fig. 4) indicate that for the current LFD method, the networks have a significant number of randomly deposited SWNTs that become less apparent as the overall density is increased. Efforts in this group currently involve increasing the precision of alignment over the entire range of densities.

One of the advantages of the LFD method is that deposition cycles can be repeated until the desired density

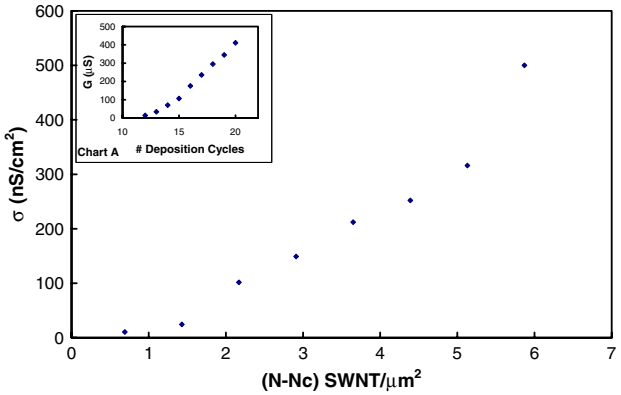

Fig. 5 Current density versus (N–N_c) for an aligned SWNT network. σ is the current density for the network. The data best fit the power law equation: $y = 18.811x^{1.8}$, with $R^2 = 0.9759$. Inset: Conductance versus number of deposition cycles for an aligned SWNT network. Macroscopic conduction began at 12 deposition cycles, with a conductance (G) of 14.65 μS. After 20 deposition cycles, the conductance reached 441.1 μS

is reached. AFM images for a sample obtained after five deposition cycles (Fig. 4a) showed the density of conducting sticks on the surface was 3.7 SWNTs/μm^2. This is typical for samples obtained after five deposition cycles. Percolation theory predicts that this density of SWNTs is too low to form a large-scale conducting network and such conduction was not observed.

Therefore, when the density of an SWNT network reaches a critical level (N_c, SWNTs/μm^2, Eq. 1) it begins to exhibit macroscopic conduction. The length, l, of the conducting sticks plays an important role in determining the macroscopic behavior of such a network; the longer the sticks are, the fewer the number required to reach the percolation threshold. Consequently, for a given average length of SWNTs, macroscopic conductivity is predicted to be largely density dependent, increasing exponentially as the density of SWNTs increases above the critical limit, N_c:

$$\sigma \propto A(N - N_c)^{\alpha} \quad (2)$$

where, A is a constant, N is the density of SWNTs (SWNTs/μm), N_c is the critical density from Eq. 1, and α is the critical exponent, which defines how the current density, σ, varies for SWNT densities above N_c. Continuous pathways do not exist and macroscopic conduction is not observed at SWNT densities below N_c. Alternatively, above N_c, the current density (σ) increases via a power law expression defined by α, the critical exponent.

Figure 5 shows the evolution of current density as a function of (N–N_c) for a network with average SWNT length, l = 0.8 μm. The data can be described by a power law equation with critical exponent, $\alpha = 1.8$, while theory predicts that α in random two dimensional network of conducting sticks is equal to 1.33 [17, 22, 23]. Macroscopic conduction began after 12 deposition cycles, increasing exponentially thereafter with successive depositions.

It is believed that the limitation of the theory contributes the most to the error in the critical exponent α [24]. The theory was proposed based on experiments on "conducting sticks," which means that all the sticks have the same conductivity. However, SWNTs statistically have 1/3 metallic tubes and 2/3 semi-conducting tubes. Also, Schottky-barriers may cause inconsistencies in conductance due to differing metallic–semiconducting junctions [25]. Additionally, as more deposition cycles are performed, metallic pathways begin to dominate, and further increasing conductance increases the last few depositions, generating a higher critical exponent. Furthermore, the effect of any residual SDS on the macroscopic conduction of these networks is under investigation in this group.

As the coverage of SWNTs increases, the density deposited with each deposition cycle is expected to decrease because of the smaller area of silane-coated surface available for SWNT adsorption. As a result, the rate at which N–N_c increase is expected in decrease at the last a few depositions, contributing to the increase of the critical exponent α.

Equation 1 dictates that N_c should decrease as the length of SWNTs increases as fewer SWNTs/μm^2 are required for macroscopic conduction. Therefore, because N is proportional to the number of deposition cycles, the LFD process is more efficient for suspensions of longer SWNTs. Although lower sonication powers result in longer SWNTs, more bundles are also observed in the network. High sonication powers have the effect of reducing bundles, but can also fracture SWNTs and lead to shorter average lengths. This group is currently determining ideal conditions for the formation of SWNT suspensions.

Summary

In conclusion, initial work has indicated that LFD is a reliable approach to room-temperature formation of aligned SWNT networks. Each deposition cycle results in a directly proportional increase in the SWNT density observed on the surface. AFM images of low-density networks show that the sample preparation method used in this group generates individual SWNTs. Studies in this group have indicated that the average length of individual SWNTs can be controlled by varying the sonication power used in forming the SWNT suspension, as previously reported in the literature [26–28]. This provides another level of control in SWNT network formation via LFD. The electronic behavior of these networks can be modeled by percolation theory, where the conduction increases according to a power law equation with the critical

exponent, $\alpha = 1.8$. Further, development of LFD methods for SWNT network formation are currently under development in this group.

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