High density films of semiconducting single-walled carbon nanotubes having a high degree of nanotube alignment are provided. Also provided are methods of making the films and field effect transistors (FETs) that incorporate the films as conducting channel materials. The single-walled carbon nanotubes are deposited from a thin layer of organic solvent containing solubilized single-walled carbon nanotubes that is spread over the surface of an aqueous medium, inducing evaporative self-assembly upon contacting a solid substrate.
References Cited

U.S. PATENT DOCUMENTS

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FIG. 15
ALIGNED CARBON NANOTUBES FOR USE IN HIGH PERFORMANCE FIELD EFFECT TRANSISTORS

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a divisional of U.S. patent application Ser. No. 14/177,828 that was filed Feb. 11, 2014, the entire contents of which are hereby incorporated by reference.

REFERENCE TO GOVERNMENT RIGHTS

This invention was made with government support under 1129802 and 0520527 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

Single-walled carbon nanotubes (SWCNTs) are key building blocks for nanoscale science and technology due to their interesting physical and chemical properties. SWCNTs are particularly promising for high speed and low power semiconductor electronics. A challenge, however, is the hierarchical organization of these building blocks into organized assemblies and, ultimately, useful devices. Ordered structures are necessary, as random network SWCNT thin films result in sub-optimal electronic properties including reduced channel conductance and mobility. Numerous techniques for aligning SWCNTs have been explored to solve this shortcoming and achieve higher conductance and mobility. These approaches can be divided into two main categories: (a) direct growth via chemical vapor deposition and arc-discharge, and (b) post-synthetic assembly. In the case of direct growth, both metallic and semiconducting SWCNTs are produced. In this case, the performance of SWCNT field effect transistors (FETs) is limited by the metallic SWCNTs (m-SWCNTs), thus motivating attempts to purify semiconducting SWCNT (s-SWCNT) samples with homogeneous electronic properties.


SUMMARY

High density films of s-SWCNTs having a high degree of nanotube alignment are provided. Also provided are methods of making the films and field effect transistors that incorporate the films as conducting channel materials.

One embodiment of a method of forming a film of aligned s-SWCNTs on a substrate includes the steps of: (a) partially submerging a hydrophobic substrate in an aqueous medium; (b) applying a dose of a liquid solution to the aqueous medium, the liquid solution comprising semiconductor-selective-polymer-wrapped s-SWCNTs dispersed in an organic solvent, whereby the liquid solution spreads into a layer on the aqueous medium at an air-liquid interface and semiconductor-selective-polymer-wrapped s-SWCNTs from the layer are deposited as a stripe of aligned semiconductor-selective-polymer-wrapped s-SWCNTs on the hydrophobic substrate; and (c) at least partially withdrawing the hydrophobic substrate from the aqueous medium, such that the portion of the hydrophobic substrate upon which the stripe of aligned semiconductor-selective-polymer-wrapped s-SWCNTs is deposited is withdrawn from the air-liquid interface. Steps (b) and (c) may be repeated one or more times in sequence to deposit one or more additional stripes of aligned semiconductor-selective-polymer-wrapped s-SWCNTs on the hydrophobic substrate.

An embodiment of a film comprising aligned s-SWCNTs, can be characterized in that the s-SWCNTs in the film have a degree of alignment of about ±15° or better and the single-walled carbon nanotube linear packing density in the film is at least 40 single-walled carbon nanotubes/μm. In some embodiments, the films have a semiconductor single-walled carbon nanotube purity level of at least 99.9%.

An embodiment of a field effect transistor includes: a source electrode; a drain electrode; a gate electrode; a conducting channel in electrical contact with the source electrode and the drain electrode, the conducting channel comprising a film comprising aligned s-SWCNTs, wherein the s-SWCNTs in the film have a degree of alignment of about ±15° or better and the single-walled carbon nanotube linear packing density in the film is at least 40 single-walled carbon nanotubes/μm; and a gate dielectric disposed between the gate electrode and the conducting channel. Some embodiments of the transistors have an on-conductance per width of at least 5 μS μm⁻¹ and an on/off ratio per width of at least 1×10⁵.
Other principal features and advantages of the invention will become apparent to those skilled in the art upon review of the following drawings, the detailed description, and the appended claims.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1. A schematic illustration of the iterative process used to fabricate a film of s-SWCNTs, driven by the spreading and evaporation of controlled doses of organic solvent at an air/water interface.

FIG. 2. Optical microscope image of narrow films (stripes) of s-SWCNTs.

FIG. 3. High resolution SEM image of stripes of s-SWCNTs.

FIGS. 4(A) and (B) AFM images of stripes of s-SWCNTs.

FIG. 5. Raman spectra of arc-discharge SWCNTs with an isolated 532 nm laser.

FIG. 6 shows the G-band of s-SWCNT arrays taken at various angles (90°, 10°, 20°, 30°, 40°, 50°, 60°, 70°, 80°, 90°, from back to front) as a function of the angle between the laser, polarization and the s-SWCNT stripe long-axis.

Inset: angular dependence of the Raman intensity at 1,594 cm⁻¹.

FIG. 7 shows the probability distribution function showing the degree of alignment of arc-discharge and HiPco s-SWCNTs.

FIG. 8 shows the comparison of dose-controlled, floating evaporative self-assembly aligned SWCNTs (this work) with other methods reported in the literature. CVD growth was used for the circles (metallic and semiconducting SWCNT are mixed) and post synthesis assembly was utilized for the squares.

FIG. 9. Output characteristics at varying gate voltages demonstrating the p-type behavior of a s-SWCNT film in a typical FET (L=9 µm, W=4 µm).

FIG. 10. Transfer characteristics demonstrating a on/off ratio of greater than 10⁶ and high current output for the typical FET.

FIG. 11. SEM image of an aligned s-SWCNT-based transistor. Scale bar is 2 µm.

FIG. 12. SEM image (scale bar=200 nm) of a 400 nm channel length FET.

FIG. 13. AFM image of an aligned s-SWCNT stripe. The inset is the film thickness profile along the dark grey cross-section.

FIG. 14. Raman map of a ~20 µm² stripe overlaying a corresponding SEM image (scale bar=1 µm). Gray scales bar indicates G-band intensity divided by SI intensity.

FIG. 15. Output characteristics of a 9 µm channel length FET at VDS=30 V (squares) to 10 V (diamonds) in 10 V increments. The inset shows the forward and backward sweep curves at VDS=1 V.

FIG. 16. Transfer characteristics of 22 different 400 nm channel length FET devices at VDS=1 V. The inset is the on/off ratio histogram.

FIG. 17. On- (squares) and off- (circles) conductance at each channel length. Median values are plotted, and the error bars indicate maximum and minimum values.

FIG. 18. Comparison of s-SWCNT FET performance (on-conductance per width versus conductance modulation) achieved in Example 2 to previous studies. Median values for this work are plotted as stars and calculated from the following number of devices at each channel length: 400 nm (22 devices), 1-2 µm (6 devices), 3-4 µm (6 devices), and 9 µm (4 devices). Error bars for this work indicate maximum and minimum values.

**DETAILED DESCRIPTION**

High density films of s-SWCNTs having a high degree of nanotube alignment are provided. Also provided are methods of making the films and field effect transistors that incorporate the films as conducting channel materials.

The films are formed using a method referred to in this disclosure as “dose-controlled, floating evaporative self-assembly”. This method uses a thin layer of organic solvent containing solubilized s-SWCNTs at an air-liquid interface to deposit films of aligned s-SWCNTs on a partially submerged hydrophilic substrate. The method decouples the s-SWCNT film formation from the evaporation of a bulk liquid medium and, by iteratively applying the s-SWCNTs in controlled “doses”, allows for the rapid sequential deposition of a series of narrow s-SWCNT films, or “stripes”, with continuous control over the width, s-SWCNT density and periodicity of the stripes. The resulting films can be characterized by a high degree of s-SWCNT alignment and high s-SWCNT densities. As a result, they are well suited for use as channel materials in FETs having high on-conductance values and high on/off ratios.

An advantage of the dose-controlled, floating evaporative self-assembly method is that it allows for the deposition of s-SWCNTs with exceptional electronic type purity—sorted using semiconductor-selective polymers—in organic solvents. Unlike anionic surfactants, which have been used to sort s-SWCNTs in aqueous solution, semiconductor-selective polymers are advantageous because they can selectively “pick out” semiconductor nanotubes directly from aqueous solutions of raw SWCNT powders, thereby avoiding the need for subsequent post-dispersion sorting.

An embodiment of the dose-controlled, floating evaporative self-assembly method is illustrated schematically in FIG. 1. As shown in panel (i) of the figure, the method begins with a hydrophilic substrate 102 partially submerged in an aqueous liquid medium 104, such as water. A dose of a liquid solution in the form of a droplet 106 is dropped into liquid medium 104, preferably in close proximity to substrate 102. The liquid solution, which is also referred to herein as an “organic ink” or a “s-SWCNT ink”, comprises s-SWCNTs 108 dispersed in an organic solvent 110. The s-SWCNTs have a semiconductor-selective polymer coated on their surfaces and are referred to herein as “semiconductor-selective-polymer-wrapped” s-SWCNTs. The liquid solution spreads (represented by solid arrows in the figure) into a thin layer over the surface of aqueous liquid medium 104 at the air-liquid interface (panel (ii)). Driven by diffusion, semiconductor-selective-polymer-wrapped s-SWCNTs 108 in the thin layer of liquid solution come into contact with and deposit onto hydrophilic substrate 102 as a stripe 112 of aligned s-SWCNTs near the air-liquid interface, while organic solvent 110 rapidly evaporates. Stripe 112 spans the width of the substrate. Without intending to be bound to a particular theory, the inventors believe that the s-SWCNTs adopt an aligned configuration because, as the solvent level rapidly decreases during evaporation, the s-SWCNTs tend to orient perpendicular to the evaporation front because that is sterically a more favored position. It is also likely that there is less of a steric penalty for the
s-SWCNTs to turn sideways, rather than for them to stand up out of the solvent layer into the air while the solvent front recedes.

Once stripe 112 has been formed, substrate 108 can be elevated such that the stripe is withdrawn from the air-liquid interface (panel (iii)). Additional doses of the liquid solution can be added sequentially and the process repeated to form a series of stripes 114 comprising aligned s-SWCNTs (panel (iv)). Using this process, very thin films of s-SWCNTs—typically having a thickness of only a monolayer or a bilayer of s-SWCNTs—can be deposited.

Optionally, the semiconductor-selective polymer can be partially or entirely removed from the s-SWCNTs after stripe formation. This can be accomplished, for example, using a polymer-selective dry or wet chemical etchant or through selective thermal decomposition of the polymer. In some embodiments of the methods, the amount of semiconductor-selective polymer on the s-SWCNTs can be reduced prior to adding them to the dose.

By controlling the velocity of the withdrawal of substrate 108, the stripe width (i.e., the dimension of the stripe that runs parallel to the direction of withdrawal), stripe periodicity and s-SWCNT density of the stripes can be carefully controlled. The optimal substrate withdrawal rate can depend on a variety of factors, including the desired characteristics of the final deposited films, the nature of the substrate and/or the rate of dose dispensation. The present methods are able to deposit stripes over a large substrate surface area rapidly, even at room temperature (about 23°C) and atmospheric pressure. For example, in some embodiments, the methods deposit stripes of aligned s-SWCNTs at a substrate withdrawal rate of at least 1 mm/min. This includes embodiments in which the substrate withdrawal rate is at least 5 mm/min. By way of illustration, using such high withdrawal rates, the present methods are able to deposit a series of stripes of aligned s-SWCNTs with a periodicity of 200 µm or less over the entire surface of a 12 inch wafer (e.g., Si wafer) in less than one hour.

The density of SWCNTs in the stripes refers to their linear packing density, which can be quantified in terms of the number of SWCNTs per µm and measured as demonstrated in Example 1, below. In some embodiments, the dose-controlled, floating evaporative self-assembly method deposits films having a SWCNT density of at least 30 SWCNTs/µm. This includes embodiments in which the films have a SWCNT density of at least 35 SWCNTs/µm, at least 40 SWCNTs/µm, at least 45 SWCNTs/µm and at least about 50 SWCNTs/µm.

The degree of alignment of the SWCNTs in the stripes refers to their degree of alignment along their longitudinal axes within a stripe, which can be quantified as demonstrated in Example 1, below. In some embodiments, the dose-controlled, floating evaporative self-assembly deposits films having a SWCNT degree of alignment of ±17° or better. This includes embodiments in which the SWCNTs have a degree of alignment of ±16° or better, and further includes embodiments in which the SWCNTs have a degree of alignment of ±15° or better.

The semiconductor-selective polymer that wraps the s-SWCNTs is present by virtue of a highly selective pre-sorting of the s-SWCNT from a starting sample containing both s-SWCNTs and m-SWCNTs. The semiconductor-selective polymers selectively attach to (e.g., adsorb on) the surfaces of s-SWCNTs relative to the surfaces of m-SWCNTs. This allows for the separation of the selectively wrapped s-SWCNTs from the m-SWCNTs using, for example, centrifugation and filtration. By pre-sorting the SWCNTs to remove m-SWCNTs, films having very high s-SWCNT purity levels can be formed, where s-SWCNT purity level refers to the percentage of SWCNTs in the film that are s-SWCNTs. For example, some of the films formed by the dose-controlled, floating evaporative self-assembly method have a s-SWCNT purity level of at least 99%. This includes films having a s-SWCNT purity level of at least 99.5% and further includes films having a s-SWCNT purity level of at least 99.9%.

A number of semiconductor-selective polymers are known. Description of such polymers can be found, for example, in Nish, A.; Hwang, J. Y.; Doig, J.; Nicholas, R. J. Highly selective dispersion of single-walled carbon nanotubes using aromatic polymers. Nat. Nanotechnol. 2007, 2, 640-6. The semiconductor-selective polymers are typically organic polymers with a high degree of π-conjugation and include polythiophene derivatives, such as poly(9,9-dialkylfluorene) derivatives, and poly(alkylvinylene) derivatives. While the semiconductor-selective polymers may be conductive or semiconductive polymers, they can also be electrically insulating.

The organic solvent desirably has a relatively low boiling point at the film deposition temperature and pressure, typically ambient temperature and pressure, such that it evaporates rapidly. In addition, it should have the capacity to solubilize the semiconductor-selective-polymer-wrapped s-SWCNTs. Examples of suitable organic solvents include chloroform, dichloromethane, N,N-dimethylformamide, benzene, dichlorobenzene, toluene and xylene.

The dose of liquid solution that contains the organic solvent and the solvated polymer-wrapped s-SWCNTs is a quantity of liquid, such as a droplet, having a volume much smaller than that of the aqueous medium to which it is delivered. By using very small volume doses to deliver the s-SWCNTs to a substrate, the present methods are able to form high density films with very small quantities of SWCNTs and organic solvents, relative to other solution-based SWCNT deposition methods. By way of illustration only, the doses used in the present methods may have a volume in the range from about 0.5 to about 50 µL. However, volumes outside of this range can be used. The concentration of SWCNTs in each dose can be adjusted to control the density of s-SWCNTs in a deposited stripe. If a plurality of stripes are deposited, the concentration of s-SWCNTs in different doses can be the same or different. By way of illustration only, the doses used in the present methods may have a SWCNT concentration in the range from about 1 to about 50 µg/mL. However, concentrations outside of this range can be used. The dose dispensation rate can be adjusted to control the periodicity of the stripes formed on a substrate. If a plurality of stripes are deposited, the dose dispensation rate can be kept constant throughout the method to provide regularly spaced stripes on a substrate. Alternatively, the dose dispensation rate can be changed throughout the method to provide stripes having different inter-stripe spacings.

The substrate onto which the films comprising aligned semiconductor-selective-polymer-wrapped s-SWCNTs are deposited are sufficiently hydrophobic that the polymer-wrapped s-SWCNTs have a higher affinity for the substrate than the aqueous medium. The hydrophobic substrates can be composed of a hydrophobic material or can comprise a hydrophobic surface coating over a support substrate. Hydrophobic polymers are examples of materials that can be used as substrate materials, including coatings. If the films
are to be used as a channel material in an FET, the substrate can comprise a gate dielectric material, such as SiO₂, coated with a hydrophobic coating.

FETs comprising the films of aligned s-SWCNTs as channel materials generally comprise a source electrode and a drain electrode in electrical contact with the channel material; a gate electrode separated from the channel by a gate dielectric; and, optionally, an underlying support substrate. Various materials can be used for the components of the FET. Example 2, below, illustrates an FET that includes a channel comprising a film comprising aligned s-SWCNTs, a SiO₂ gate dielectric, a doped Si layer as a gate electrode and metal (Pd) films as source and drain electrodes. However, other materials may be selected for each of these components. Channel materials comprising the highly aligned s-SWCNTs having high s-SWCNT purity levels and high SWCNT density are able to provide FET characteristics by both high on-conductance per width \( G \) and on/off ratio. For example, some embodiments of the FETs have an on-conductance per width of at least 5 \( \mu S \) \( \mu m^{-1} \) and an on/off ratio per width of at least 1 \( \times 10^5 \). These performance characteristics can be achieved with channel lengths in the range from, for example, about 400 nm to about 9 \( \mu m \), including channel lengths in the range from about 1 \( \mu m \) to about 4 \( \mu m \). For example, as illustrated in Example 2, below, some embodiments of the FETs having a channel length of a few hundred nanometers to about 400 nm are able to provide on-conductance per width greater than 60 \( \mu S \) \( \mu m^{-1} \) and an on/off ratio per width of at least 2 \( \times 10^7 \), while some embodiments of the FETs having a channel length of at least 9 \( \mu m \) are able to provide on-conductance per width greater than 7 \( \mu S \) \( \mu m^{-1} \) and an on/off ratio per width of at least 2 \( \times 10^9 \).

**EXAMPLES**

**Example 1**

In this example, arrays of parallel strips comprising aligned s-SWCNTs with exceptional electronic-type purity levels (99.9% s-SWCNTs) were deposited at high deposition velocities using the dose-controlled, floating evaporative self-assembly process with control over the placement of the stripes and the quantity of s-SWCNTs. By decoupling the s-SWCNT stripe formation from the evaporation of the bulk solution and by iteratively applying the s-SWCNTs in controlled doses, the dose-controlled, floating evaporative self-assembly process formed stripes in which the s-SWCNTs were aligned within ±14°, were packed at a density of ~50 s-SWCNTs \( \mu m^{-1} \), and constituted primarily a well-ordered monodisperse layer. FET devices incorporating the stripes showed high performance with a mobility of 38 cm² V⁻¹ s⁻¹ and on/off ratio of 2.2 \( \times 10^5 \) at a 9 \( \mu m \) channel length.

Results and Discussion

Two different types of s-SWCNT inks were examined. The first type of ink was processed from arc-discharge SWCNT powders (Nano Lab, Inc.). In this case, the polyfluorene derivative poly[(9,9-diocnylfluorenyl-2,7-diy1)-alt-co-(6,6'-[2,2'-bipyridine])]) (PFO-BPy), was employed as a semiconductor-selective polymer. PFO-BPy has been shown to selectively wrap highly semiconducting SWCNT species. (See, Misra, K. S.; Larsen, B. A.; Blackburn, J. L. High-Yield Dispersions of Large-Diameter Semiconducting Single-Walled Carbon Nanotubes with Tunable Narrow Chirality Distributions. ACS Nano 2013, 7, 2231-2239.) The arc-discharge powder and PFO-BPy were dispersed in toluene by ultrasonication where the PFO-BPy wrapped s-SWCNTs were solubilized, while leaving the remaining carbon residuals and m-SWCNTs in large bundles and aggregates, which were removed by centrifugation. Absorption spectra of the sorted and unsorted SWCNT solutions were obtained for comparison. Metallics peaks present in the unsorted spectra around 700 nm were absent after sorting with PFO-BPy. Following the initial sorting process excess polymer chains were removed by repeated dispersion and centrifugation of the SWCNTs in tetrahydrofuran. The second type of ink was processed from high pressure carbon monoxide (HipCO) produced powders (Nanointegris Inc.). In this case the polyfluorene derivative poly[(9,9-di-n-octylfluorenyl-2,7-diy1)] (PFO) was used as a semiconductor-selective polymer. (See, Nish, A.; Hwang, J. Y.; Doig, J.; Nicholas, R. J. Highly selective dispersion of single-walled carbon nanotubes using aromatic polymers. Nat. Nanotechnol. 2007, 2, 640-6.)

**FIG. 1** is a schematic illustration of the method. A 2 µl dose of >99.9% purified arc discharge s-SWCNT ink in chloroform (concentration=10 µg ml⁻¹) was dropped onto the water surface 0.5 cm away from the vertically oriented substrate as shown in panel (i) of FIG. 1. The dose covered the water surface by spreading at the air/water interface and reached the substrate quickly as a result of surface tension effects (panel (ii) in FIG. 1). Chloroform was chosen as a suitable solvent for this study as it spreads and evaporates rapidly across the water surface.

It should be noted that unlike previous studies on evaporative self-assembly from aqueous solutions of SWCNTs where low pressure was required to speed up the evaporation of water and hence the assembly process, the use of high vapor pressure organic solvents in this example allows for much more rapid assembly under ambient conditions. For example, a deposition velocity of 5 mm min⁻¹ at ambient conditions is demonstrated here. Reported deposition velocities using standard evaporative self-assembly from aqueous solutions are much slower, only 0.02 and 0.001 mm min⁻¹ at 70 and 760 Torr, respectively, using similar substrate dimensions. As the organic ink spreads, it comes in contact with the partially submerged substrate. Subsequent rapid evaporation of the chloroform (FIG. 1, panel (ii)) results in the formation of a stripe of aligned s-SWCNTs on the vertically submerged substrate. As the solvent level rapidly decreases during evaporation, the s-SWCNTs tend to orient perpendicular to the evaporation front, which is sterically a more favored position.

The results of these experiments showed the formation of continuous stripes of aligned s-SWCNTs (FIG. 1, panels (iii) and (iv)) and demonstrated the ability to control three pivotal factors: (1) the width of the stripes, (2) the density of SWCNTs within each stripe, and (3) the spacing between the stripes. Control over the width of the stripes by varying the substrate elevation velocity was demonstrated. For a dose concentration of 10 µg ml⁻¹, at a high velocity of 9 mm min⁻¹ the SWCNTs became randomly dispersed while at 1 mm min⁻¹ they began to aggregate into large bundles or ropes. At an optimized velocity of 5 mm min⁻¹, the s-SWCNTs in the resulting stripes were well isolated from one another and well aligned. FIG. 2 shows an optical micrograph of aligned s-SWCNT stripes with widths of 20 ± 2.5 µm fabricated under these optimized conditions. By optimizing the elevation velocity the width of the stripes could...
be dictated. Another crucial factor for scalable electronics is controlling the stripe spacing. To demonstrate periodic stripe spacing, a constant substrate elevation velocity of 5 mm min\(^{-1}\) was set and one dose per 1.2 sec was applied to achieve a stripe periodicity of 100 µm (FIG. 2). With this method it is possible to fabricate aligned SWCNT arrays with control over the stripe width, stripe periodicity, and SWCNT density, in a continuous manner, which makes this appealing for high throughput microelectronic applications. The substrates used here were treated with a Piranha solution of H\(_2\)O\(_2\) (33%) concentrated H\(_2\)SO\(_4\) (67%) followed by vapor deposition of a hexamethyldisilazane self-assembling monolayer to increase the hydrophobicity of the SiO\(_2\) surface. Unlike previous studies on evaporative self-assembly from aqueous solutions of SWCNTs, which worked well on hydrophilic substrates, this method using organic solutions gave the best results on HMDS treated substrates. HMDS treated substrates may be advantageous for TFT devices as they lead to lower charged impurity concentrations.


The r for both types of s-SWCNTs aligned by this method was measured. For s-SWCNTs of diameter 0.8-1.1 nm produced by the HiPco method, r=15.8 corresponding to α=31°. For s-SWCNTs of diameter 1.3-1.7 nm produced by the arc-discharge method, r=3.47 corresponding to α=14.41°. The degree of alignment of arc-discharge s-SWCNTs was significantly better than HiPco s-SWCNTs likely because the arc-discharge s-SWCNTs were stiffer (due to their larger diameter). The average length of the arc-discharge and HiPco s-SWCNTs were 465.5 and 449.1 nm, respectively, as determined by AFM. The similarity in length suggests that the improved alignment of the arc-discharge SWCNTs may be solely a result of the structural rigidity. Alignment imperfections existed in both HiPco- and arc-discharge s-SWCNT assemblies, which included voids, bending defects, and randomly oriented SWCNTs. However, defects due to bending and looping of nanotubes were associated more with HiPco s-SWCNTs. The degree of alignment of the arc-discharge s-SWCNTs here is compared to other reported methods with comparable s-SWCNT den-
Preparation of Semiconducting SWCNTs

Arc-Discharge: Mixtures of arc-discharge SWCNT powders (2 mg ml\(^{-1}\)) and PFO-BPy (American Dye Source, 2 mg ml\(^{-1}\)) were sonicated for 30 min in toluene (30 ml). The solution was centrifuged in a swing bucket rotor at 50,000 g for 5 min, and again at 50,000 g for 1 hr. The supernatant was collected and filtered through a syringe filter. A distillation removed toluene over a 30 min duration. The residue of PFO-BPy and s-SWCNTs were dispersed in tetrahydrofuran (THF). The s-SWCNT solution in THF was centrifuged at 15,000 g for 12 hours. The supernatant (excess PFO-BPy) was discarded and the pellet was dispersed into THF. After removing the THF, the residue was dispersed in chloroform to a concentration of 10 \(\mu\)g ml\(^{-1}\).

HiPco:
The initial dispersion of HiPco (Nanointegris Inc.) SWCNTs were prepared using 2 mg ml\(^{-1}\) of HiPco powder and 2 mg ml\(^{-1}\) of PFO (American Dye Source) in toluene. The same sonication, centrifugation, and dried methods as for arc-discharge SWCNTs were used for the dispersion of s-SWCNTs, separation of unwanted material, and removal of excess polymer.

Raman Spectroscopy Characterization:
Raman characterization was measured in a confocal Raman microscope with laser excitation wavelength of 532 nm (Aramis Horiba Jobin Yvon Confocal Raman Microscope). The device was equipped with a linear polarizing filter between the sample and the incident beam laser to allow polarization-dependent measurements.

Imaging:
SEM images were collected with LEO-1530 field-emission scanning electron microscope (FE-SEM). The surface morphology of the s-SWCNTs was imaged using a Nanoscope III Multimode atomic force microscope (Digital Instruments). Imaging mode was utilized for the AFM measurement. A triangular cantilever with an integral pyramidal Si\(_3\)N\(_4\) tip was used. The typical imaging force was of the order of 10\(^{-7}\) N.

Langmuir-Blodgett Trough and Substrate:
The LB trough (KSV NIMA Medium size KN 2002) was primarily used as a trough to spread s-SWCNTs at 23°C with Wilhelmy balance (Platinum plate). Milli Q water (resistively ca. 18.2 M\(\Omega\) cm) was used as the water substrate. The Si/SiO\(_2\) substrates were cleaned by a Piranha solution of H\(_2\)O\(_2\) (33%/v/v)/H\(_2\)SO\(_4\) (67%/v/v) for 30 min and rinsed with deionized (DI) water. After Piranha treatment, the substrates were covered by a hexamethyldisilazane self-assembling monolayer (vapor deposition).

FET Fabrication:
First, stripes of arc-discharge s-SWCNTs were deposited on a highly doped Si substrate with a 90 nm thermally grown SiO\(_2\), which served as the backgate electrode and dielectric, respectively. Electron beam lithography was then used to clean the stripes so that they had a length of 20 \(\mu\)m. Samples were then annealed in a mixture of a99.999% Ar (95%): H\(_2\) (5%) in order to partially degrade the PFO-BPy polymer, followed by annealing in vacuum at 1\(\times\)10\(^{-7}\) Torr and 400°C for 20 min. A second electron beam lithography step was used to define the top-contacted electrodes. Thermal deposition of Pt (40 nm) was used to create source and drain contacts to the s-SWCNT stripe. Finally, the devices were annealed in argon atmosphere at 225°C.

Example 2

This example illustrates the performance of exceptionally electronic-type sorted, aligned s-SWCNTs in field effect...
transistors. High on-conductance and high on/off conductance modulation are simultaneously achieved at channel lengths that are both shorter and longer than individual s-SWCNTs. The s-SWCNTs were isolated from heterogeneous mixtures of s-SWCNTs and m-SWCNTs using a polyfluorene-derivative as a semiconductor selective agent and aligned on substrates via dose-controlled, floating evaporative self-assembly.

Example 1 illustrates that s-SWCNTs isolated from polydispersity mixtures of SWCNTs using the polyfluorene-derivative poly([9,9-diocetylfluorenyl-2,7-diyl]-alt-co-[6,6'-2,2'-bipyridine]-),PFO-BPy) as a sorting agent can be aligned on substrates via dose-controlled, floating evaporative self-assembly. This example evaluates the performance of these aligned s-SWCNTs as channel materials in FETs and reports exceptionally high on/off conductance modulation and on-conductance, over a range of channel lengths, compared to previous reported studies.

High purity s-SWCNTs were extracted from an as-produced arc-discharge synthesized SWCNT powder purchased from NanoLab Inc. s-SWCNTs were isolated by dispersing the powder in a solution of PFO-BPy in toluene adapting procedures reported by Mistry et al. During the initial dispersion process the polymer selectively wraps and solubilizes predominantly semiconducting species. Excess polymer was removed by dispersing the s-SWCNTs in tetrahydrofuran followed by repeated sedimentation and dispersion cycles, which effectively removed polymer chains that were not tightly bound to the s-SWCNT surface. Removing excess polymer improved the self-assembly of aligned s-SWCNT arrays and improved the contact of s-SWCNT to metal electrodes in FETs for higher performance.

Optical absorption spectra of sorted and unsorted PFO-BPy SWCNT solutions were obtained for comparison. In both the sorted and unsorted spectra the S_{21} optical transitions were broadened around a wavelength of 1050 nm due to the overlap of peaks from a chiral distribution of s-SWCNTs with diameters 1.3-1.7 nm. Previous investigations have used photoluminescence and Raman spectroscopy to confirm that PFO-BPy differentiates by electronic type, but not strongly by diameter, thus resulting in diameter distributions that match the s-SWCNT starting material. The broad M_{11} peak, which is visible in the unsorted spectra is immeasurable after sorting suggesting a purity of >99%. The features from 400-600 nm are combinations of the S_{13} s-SWCNT transitions coupled with absorption from the PFO-BPy, which is centered at 560 nm.

For the FET devices, highly doped Si substrates with a 90 nm thick SiO_{2} dielectric layer were used as the gate electrode and dielectric, respectively. Prior to s-SWCNT deposition, the substrates were treated with a solution of 20 ml H_{2}SO_{4}:10 ml H_{2}O_{2} followed by vapor deposition of a hexamethyldisilazane self-assembly monolayer to increase the hydrophobicity of the SiO_{2} surface. The dose-controlled, floating evaporative self-assembly procedure is described briefly below and in detail in Example 1, above. Droplets (“doses”) of a solution of 10 \mu g ml^{-1} s-SWCNTs in chloroform were cast on a water trough. The s-SWCNTs spread across the surface of the water and deposited on the substrate which was slowly extracted from the trough, normal to the air-water interface. Each droplet created a well-aligned stripe of s-SWCNTs across the entire width of the substrate. Here, periodic arrays of stripes were achieved by successively adding droplets to the through surface at 12 second intervals as the substrate was elevated at a constant rate of 5 mm min^{-1}.

The uniformity, density, and thickness of s-SWCNTs in a single stripe were characterized using SEM, AFM and Raman spectroscopy (FIGS. 12, 13 and 14, respectively). The AFM thickness profile shown in FIG. 13 varies between 2-4 nm, indicating for the most part that each stripe is composed of single layers of s-SWCNTs with localized regions of inter-nanotube overlap. The G-band Raman intensity (3 mW, 532 nm) of the s-SWCNTs is spatially mapped for one stripe in FIG. 14, normalized to the substrate Si peak intensity. The G-band intensity varies only by ±12.5% indicating that the density of the s-SWCNTs within each stripe was fairly uniform. SEM images (example presented in FIG. 12) were used to quantify a s-SWCNT linear packing density of 40-50 s-SWCNTs mm^{-1}. These measurements indicated that the stripes were monolayers of well-isolated s-SWCNTs with occasional inter-nanotube overlap from randomly oriented s-SWCNTs. These results indicate that interweave into the well-ordered s-SWCNTs at a linear occurrence of one randomly oriented s-SWCNT per two micrometers. The randomly overlapping nanotubes may be beneficial in establishing inter-SWCNT connectivity in the FET percolation regime where channel length (L_{c}) is much greater than the s-SWCNT length (L_{c} <= L_{0}).

FETs were fabricated from the stripes using electron beam (e-beam) lithography. The stripes varied in width from 10-20 \mu m. Therefore, they were lithographically patterned to ensure a consistent FET channel width of 4 \mu m. First, e-beam patterning was used to expose regions around the s-SWCNT stripes where unwanted s-SWCNTs were to be removed and etching via a 20 s exposure to an oxygen plasma (50 W, 10 mTorr, and 10 sccm O_{2}, flow rate) was used. To remove PMMA resist, films were developed in acetone and toluene each for 30 minutes at 60°C. and rinsed in isopropyl alcohol. Samples were then annealed in 99.9999% Ar (95%), H_{2} (5%) at 500°C, to partially remove and decompose the PFO-BPy. An additional annealing step was conducted in high vacuum at 1 x 10^{-7} Torr at 400°C for 20 minutes to further degrade and partially remove polymer residue. A second e-beam step defined the source-drain electrodes and contact pads. The pattern was developed to remove resist and the underlying electrode pattern was exposed to ultraviolet light in air at a power of 0.1 W cm^{-2} for 90 s (SCD88-9102-02 BHK Inc.) to improve adhesion of Pt to the SWCNT surface. Thermal evaporation of a 40 nm thick layer of Pt defined the source-drain electrodes, followed by lift off, which was achieved by soaking samples in acetone at 120°C for 5 minutes and bath sonication in acetone for 30 seconds. Immediately before measurement the devices were annealed at 225°C in Ar to improve contact resistance. The resulting device architecture of a 400 nm device is shown in FIG. 12.

The electronic characteristics of s-SWCNT channel FETs were measured using a Keithley source meter instrument (Model 2636A). Measurements were made on devices of varying channel length in order to quantify transport properties in both the direct and percolative regimes and to assess the electronic-type purity of the s-SWCNTs. The characteristics of a typical 9 µm channel length device (in the percolating regime) are shown in FIG. 15, demonstrating the p-type behavior of the aligned s-SWCNTs. At low fields the current output followed linear behavior indicating ohmic contact at the Pt-SWCNT interface. The transfer characteristics are shown in the insert. Hysteresis typical of SWCNT-based devices that are not treated to remove the surface adsorbrates was observed. The on/off ratio of the device was 5x10^{5}. The on-conductance was 7.3 µS µm^{-1}, which corre-
sponds to a field-effect mobility of 46 cm²V⁻¹s⁻¹, applying a standard parallel plate capacitance model:

\[ \mu = \frac{L_{\text{eff}}}{\epsilon_{\text{SiO}_2} \cdot \text{p}_{\text{SiO}_2}} \cdot \frac{\Delta I}{\Delta V} \]  

(3)


On-conductance as high as 240 μS μm⁻¹ has been reported for SWCNT FETs in the direct transport regime, however, the on/off ratio in such devices was limited to ~10⁵, presumably by the presence of metallic nanotubes. Similarly, in the percolative regime, high on/off ratios on the order of 10⁶ have been achieved, but devices were limited by an on-conductance of ~4 μS μm⁻¹ for channel length of ~5 μm. Due to the number of percolation pathways in network s-SWCNT FETs or the low density of s-SWCNTs in aligned CVD-films. For example, it has been challenging to achieve both high on-conductance and on/off ratio simultaneously in the percolative regime. (See, for example, D. M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nabiulbin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, Nat. Nanotechnol. 6 (3), 156 (2011) and S. H. Jia, S. N. Dunham, J. Song, X. Xie, J. H. Kim, C. Lu, A. Islam, F. Du, J. Kim, J. Felts, Y. Li, F. Xiong, M. A. Wahab, M. Menon, E. Cho, K. L. Grosse, D. J. Lee, H. U. Chung, E. Pop, M. A. Alam, W. P. King, Y. Huang, and J. A. Rogers, Nat. Nanotechnol. 8 (3), 347 (2013)).

Here, high on-conductance and high on/off ratio were achieved simultaneously. At a channel length of 400 nm in the direct regime, an on-conductance per width as high as 61 μS was achieved, while maintaining a median on/off ratio of 2×10⁸. At a channel length of 9 μm in the percolative regime, a median on/off ratio of 2×10⁸ was achieved, while reaching conductance values as high as 7.5 μS μm⁻¹. At intermediate channel lengths ranging from 1-4 nm the achieved on-conductance and on/off ratio fell in between these two cases along an inversely sloping line in FIG. 18. In general, the performance of the present devices pushes out further to the upper-right corner of the graph in FIG. 18 than any of the other families of devices, extending further in on-conductance and on/off ratio than these previous studies.

The high on-conductances and on/off ratios likely originate from a combination of factors including (a) the high semiconducting purity of the s-SWCNTs and (b) their high degree of alignment. An additional factor may be attributed to (c) a reduction in inter-nanotube charge screening due to the presence of the polymer wrapping s-SWCNT deposition which reduces s-SWCNT bundling and interactions. To test factor (a), 22 different FET devices with channel lengths of 400 nm were measured. The analysis of the individual s-SWCNT length distribution presented in Example 1 indicated that roughly half of the individual s-SWCNTs were longer than 400 nm. Thus, these 400 nm FETs provided a sensitive measure of the presence of metallic SWCNTs. These FETs were composed of 4,071 individual s-SWCNTs or small pairs or bundles of s-SWCNTs. The conductance modulation of each FET (FIG. 16) was used to estimate the electronic-type purity of the SWCNTs within the FET, where the presence of even a single metallic nanotube directly spanning the channel will cause a substantial increase in the on-conductance on the order of 1-10 μS. The median on-conductance was 130 μS, therefore an on/off ratio for a FET containing a single metallic nanotube that spans the channel was expected to be reduced to the order of 10⁻¹⁰. Of the devices measured, the lowest on-conductance was 6.8×10⁶, nearly two orders of magnitude larger than the highest on/off ratio expected for a device containing a single metallic nanotube. The median on-conductance was 2×10⁵ with only three devices having on/off ratios lower than 10⁴. If half of the 4,071 species were individual SWCNTs that fully span the channel, which is a reasonable estimate based on the measurements of length distributions in Example 1, the semiconducting purity of the sorted SWCNTs here was ~99.95%.

While factor (b) was confirmed by the SEM images, factor (c) was assessed as follows. The average inter-SWCNT spacing was ~20 nm, and the presence of bundles in solution was minimal due to the high solubility of PFO-BPy s-SWCNTs in chloroform. The stability of the PFO-BPy wrapping around s-SWCNTs may limit inter-SWCNT interactions during drying thereby creating aligned films of s-SWCNTs with less charge screening interactions.
limit the invention to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the invention. The embodiments were chosen and described in order to explain the principles of the invention and as practical applications of the invention to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended here and their equivalents.

What is claimed is:

1. A field effect transistor comprising:
a source electrode;
a drain electrode;
a gate electrode;
a conducting channel in electrical contact with the source electrode and the drain electrode, the conducting channel comprising a film comprising aligned s-SWCNTs; and
a gate dielectric disposed between the gate electrode and the conducting channel,
wherein the field effect transistor has a channel length of up to about 9 μm and an on-conductance per width of at least 5 μS μm⁻¹ and an on/off ratio per width of at least 1x10⁵.

2. The transistor of claim 1 having an on-conductance per width of at least 7 μS μm⁻¹ and an on/off ratio per width of at least 1.5x10⁵.

3. The transistor of claim 1 having an on-conductance per width of at least 10 μS μm⁻¹ and an on/off ratio per width of at least 2x10⁵.

4. The transistor of claim 1, wherein the single-walled carbon nanotube linear packing density in the film is at least 40 single-walled carbon nanotubes/μm.

5. The transistor of claim 1, wherein the single-walled carbon nanotube linear packing density in the film is at least 50 single-walled carbon nanotubes/μm.

6. The transistor of claim 1, wherein the film has a semiconducting single-walled carbon nanotube purity level of at least 99.9%.

7. The transistor of claim 1, wherein the s-SWCNTs are wrapped in a semiconductor-selective polymer.

8. The transistor of claim 1, wherein the single-walled carbon nanotube linear packing density in the film is at least 50 single-walled carbon nanotubes/μm, the film has a semiconducting single-walled carbon nanotube purity level of at least 99%, the transistor has a channel length in the range from 400 nm to 4 μm, and the transistor has an on-conductance per width of at least 10 μS μm⁻¹ and an on/off ratio per width of at least 1x10⁵.

9. The transistor of claim 1, wherein the single-walled carbon nanotube linear packing density in the film is at least 50 single-walled carbon nanotubes/μm, the film has a semiconducting single-walled carbon nanotube purity level of at least 99%, the transistor has a channel length of no greater than 400 nm, and the transistor has an on-conductance per width of at least 20 μS μm⁻¹ and an on/off ratio per width of at least 1x10⁵.

10. The transistor of claim 1, wherein the thickness of the film corresponds to no more than a bilayer of the s-SWCNTs.

11. A field effect transistor comprising:
a source electrode;
a drain electrode;
a gate electrode;
a conducting channel in electrical contact with the source electrode and the drain electrode, the conducting channel comprising a film comprising aligned s-SWCNTs; and
a gate dielectric disposed between the gate electrode and the conducting channel,
wherein the field effect transistor has a channel length of at least 9 μm and an on-conductance per width of at least 5 μS μm⁻¹ and an on/off ratio per width of at least 1x10⁶.

12. The transistor of claim 11, wherein the single-walled carbon nanotube linear packing density in the film is at least 40 single-walled carbon nanotubes/μm.

13. The transistor of claim 11, wherein the single-walled carbon nanotube linear packing density in the film is at least 50 single-walled carbon nanotubes/μm.

14. The transistor of claim 13, wherein the film has a semiconducting single-walled carbon nanotube purity level of at least 99.9%.

15. The transistor of claim 11, wherein the film has a semiconducting single-walled carbon nanotube purity level of at least 99.9%.

16. The transistor of claim 1, wherein the s-SWCNTs are wrapped in a semiconductor-selective polymer.

17. The transistor of claim 1, wherein the source electrode and the drain electrode are metal electrodes.

18. The transistor of claim 11, wherein the source electrode and the drain electrode are metal electrodes.

19. The transistor of claim 9, wherein the transistor has an on-conductance per width of at least 60 μS μm⁻¹ and an on/off ratio per width of at least 2x10⁴.

20. The transistor of claim 11, wherein the transistor has an on-conductance per width of at least 7 μS μm⁻¹ and an on/off ratio per width of at least 2x10⁴.

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