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Aligned single-walled carbon nanotube patterns with nanoscale width, micron-scale length and controllable pitch

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Abstract

We have successfully aligned single-walled carbon nanotubes (SWNTs) in patterns with nanoscale width, micron-scale length and controllable pitch on SiO₂/Si substrates using a poly(dimethylsiloxane) (PDMS) microchannel mold. The microchanneled mold was patterned with a funnel-shaped channel to minimize nanotube jamming during capillary-driven inflow. Two (i.e. pre- and post-capillary) gas blows were employed to improve nanotube alignment. The fluidically pre-aligned carbon nanotubes were 'gas-spun' into a long 20 nm wide pattern, significantly narrower than the fluidic pre-alignment channel. These narrow and long aligned SWNT patterns were successfully transferred to a pair of gold electrodes spaced 15 μm apart. The performance of the carbon nanotube field effect transistor (CNTFET) fabricated by this technique was evaluated.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional (1D) nanostructures, including carbon nanotubes (CNTs), nanowires (NWs) and nanorods, are anticipated to be key constituents in future nanoscale devices, such as molecular field-effect transistors (mFETs) [1–5], high sensitivity chemical and biological sensors [6–9] and nanoprobe [10]. One of the key challenges in developing nanoscale devices is the lack of a convenient and parallel method for large-scale assembly and alignment of 1D nanostructures into complex patterns or structures. Over the past few years, various methods such as fluidic flow-directed assembly [11–13], Langmuir–Blodgett (LB) assembly [14–16] and electric- or magnetic-field alignment [17–20], have

been developed to controllably manipulate nanotubes and nanowires.

Single-walled carbon nanotubes (SWNTs), discovered in 1993 [21, 22], are anticipated to replace silicon in future mFETs because of their nanoscale diameter, superior electronic mobility, physical properties (such as high flexibility, strength, thermal and chemical inertness) and semiconducting behavior [23, 24]. One-dimensional electron transport in SWNTs implies that their alignment to the device electrodes affects the performance of SWNT FETs. Solution-based alignment and/or patterning techniques, typically conducted at mild temperatures and environments, are applicable to substrates with limited thermal and chemical stabilities, particularly plastics, and allow for post-synthetic SWNT processing and purification [25]. For nanoelectronic devices, the SWNT pattern should ideally be confined to nanoscale width to achieve device miniaturization with minimum contamination of other areas. A precise and parallel

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deposition method to achieve SWNT arrays with controllable density, orientation, position, pattern width and separation (pitch) on electrodes is still lacking; few techniques can achieve narrow (nanosized) patterns placed at controllable positions with precise pitch/separation [26].

The LB technique [27–29] has been used to deposit single or multiple layers of functionalized carbon nanotubes (CNTs) but has not proved useful in depositing the low areal density of CNTs needed for many electronics applications. Another method is to use atomic force microscopy (AFM) to control the position and shape of individual CNTs on the surface of source and drain electrodes [30, 31]. However, the AFM method is too time-consuming for large-scale alignments of CNTs. Electric fields have been utilized to align solvent-dispersed SWNTs and multi-walled nanotubes in specific locations [32]. However, electric-field-assisted deposition methods require pre-patterned electrodes which, in some cases, have to be removed before actual electrode fabrication; further, precise control of one SWNT/bundle between electrodes and good reproducibility are both difficult since nanotubes have varying electronic properties and separation of these is difficult.

Lieber *et al* [12] used microfluidic alignment combined with serial electron beam patterning to produce aligned relatively rigid nanowires. Several groups have also used microfluidic flow to pattern and align SWNTs [33–36]. Park *et al* [37] recently demonstrated a method for *in situ* flocculation and patterning of SWNTs by inter-diffusion of two laminar liquid streams in micron-scale fluidic channels. However, the CNT patterns obtained are typically of micron scale. Others have used patterns of hydrophilic and hydrophobic areas to control the deposition of SWNT suspension on the hydrophilic areas with pattern widths of several microns; these hydrophilic/hydrophobic regions are typically patterned by contact printing which cannot easily achieve nanoscale dimensions [38]. Furthermore, the flexible SWNTs deposited tend to curl and are of high areal density. Both Lay [25] and Hedberg [39] have used gas blowing to align SWNTs on a flat Si wafer surface. Though they were able to align many tubes along the blow direction and the SWNTs deposited were relatively long (around 5–10 μm), gas blow by itself has difficulty controlling the width and pitch of SWNT patterns; low areal density SWNTs deposit over micron-scale rather than nanoscale areas. In addition, their method may not directly be applicable to the rough surfaces of wafers pre-patterned with Au electrodes which protrude from the surface.

We have previously reported a novel method of fluidic alignment for producing patterns of slightly less than 1 μm width of horizontally aligned chopped SWNTs [40, 41]. When the microchannels used for aligning the SWNTs have constant widths of slightly less than 1 μm , the resulting SWNT pattern has a minimum width also of about 1 μm and the SWNTs a modest length (0.5–1.0 μm). SWNTs which are long compared with the channel width cannot flow into the channels and instead accumulate at the channel entrance, creating a ‘log-jam’ that blocks the channel entrance. Typically, the SWNTs are chopped into short segments to reduce the ‘log-jam’ effect. However, chopping affects the electronic properties of the SWNTs and the channel width cannot be much narrower than the SWNT length; the combination of these sets a minimum width on SWNT pattern features made in this way. We have

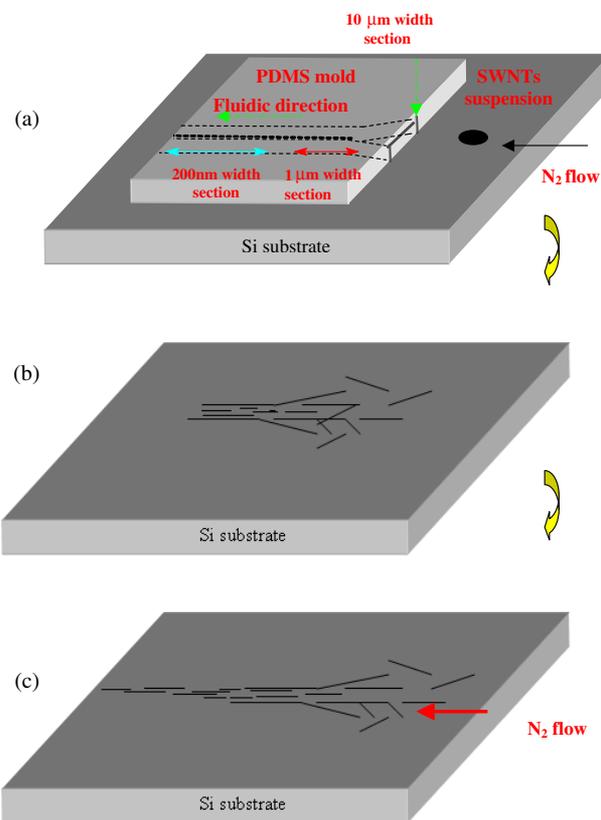


Figure 1. Schematic outline of the experiment procedure: (a) CNT solution placed near the wide end of the channel and aligned/moved toward the channel with a jet of N_2 ; (b) CNTs partially aligned/moved by capillary action after removal of the PDMS channel; (c) CNTs aligned in a narrower pattern with a second N_2 flow.

also reported [40] use of a 2D ‘funnel’ in our fluidic alignment technique to reduce the ‘log-jam’; the SWNTs are initially drawn into the wide (i.e. 1 mm) end of the channels without jamming and are then drawn into the narrow (i.e. 1 μm) part of the channel. The SWNTs can be longer (2–4 μm) but the SWNT pattern is still restricted to a minimum width of about 1 μm .

In this paper, we report a new method of gas-assisted microfluidic alignment (GAMA) to pattern and deposit SWNT patterns with nanoscale width, micron-scale length and controllable pitch. A schematic of the GAMA process is shown in figure 1. Our previously reported fluidic alignment method is supplemented with two gas blows; one before the capillary alignment for pre-alignment of the SWNTs and another after the capillary alignment for narrowing the SWNT pattern from around 1 μm to 20 nm wide. Funnel-shaped channels varying in width from 10 μm to 200 nm over 2 mm length replicated in poly(dimethylsiloxane) (PDMS) (figure 2) are used for the fluidic alignment. The PDMS mold is made hydrophilic by slight argon plasma etching and placed with the channels downwards on a flat SiO_2/Si substrate. A drop of SWNT solution is placed near the funneled end of the channels. A first gas blow over the droplet using N_2 is used to pre-align the nanotubes and push the droplet into contact with the channel entrances. At contact with the channel entrances, the SWNT solution is drawn into the funnels by capillary attraction. The

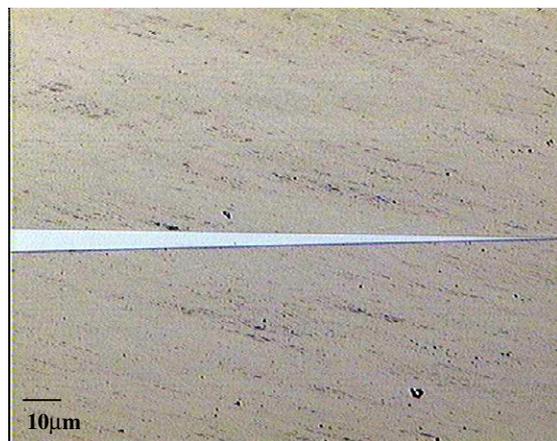


Figure 2. Optical image of 2D funnel-shaped microchannel in PDMS.

PDMS mold is then removed and the nanotube suspension is left to dry slightly and then second-time gas blown again to 'draw out' the nanotubes.

As a demonstration of the potential application of GAMA to device fabrication, the above procedure was repeated using a PDMS substrate instead; the PDMS was then used to precisely transfer print the aligned SWNT pattern onto a pair of Au electrodes spaced 15 μm apart to form a CNTFET. The CNTFET device performance was measured.

2. Experimental details

2.1. Preparation of SWNT suspension

About 30 mg of SWNTs (from Chengdu Organic Chemicals Co. Ltd China) was refluxed in 40 ml of 2.6 M HNO_3 for 10 h. The solid was collected and rinsed with deionized (DI) water on a 0.2 μm -pore PTFE membrane filter. The purified SWNTs comprising both metallic and semiconductive nanotubes with lengths of 2–4 μm were dispersed in an aqueous sodium dodecyl sulfonate solution (SDS 2 wt%). The suspension was sonicated with a probe sonicator (20 W power) for 30 min and centrifuged at 10 000 rpm (12 000 g) for 1 h. The SWNT concentration was calculated from the weights of nanotubes added and settled after centrifugation to be about $3 \times 10^{-3} \text{ mg ml}^{-1}$. Before each use, the suspension was centrifuged at 10 000 rpm for 1 h and the supernatant SWNT suspension was collected for the experiment.

2.2. PDMS channel preparation

To fabricate the PDMS microchannels, a mixture consisting of 10:1 PDMS Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 (Dow Corning Corporation, Midland, MI) was mixed thoroughly and degassed in a vacuum chamber. The prepolymer mixture was coated onto a silicon wafer master having a 2D funnel-shaped grating with 200 nm to 10 μm width and $\sim 1 \mu\text{m}$ depth (figure 2). The silicon master was patterned using thermal oxidation combined with a photolithography technique. After curing at 90 $^\circ\text{C}$ for 24 h, the PDMS mold was cooled to room temperature and then

carefully peeled from the master. Subsequently, the PDMS molds were cleaned in successive ultrasonic baths of water mixed with acetone and ethanol and then dried at 100 $^\circ\text{C}$ for 1 h. Before use, both ends of the PDMS molds containing the funnel-shaped microchannel entrances were cleanly cut to ensure the channels were open. Ar-plasma treatment was carried out in a March PX-500TM Cleaning System (March Plasma Systems, Concord, CA) operated at a radio frequency (RF) of 13.56 MHz. The microchannels were exposed to Ar plasma (Ar flow rate 350 sccm, discharge power 100 W) for 2 min and then aged in air for 30 min to acquire a temporarily hydrophilic surface character to promote wetting by the SWNT suspension. The treated molds were used immediately.

2.3. SiO_2/Si substrate preparation

SiO_2/Si wafer substrate was cut into small pieces of dimensions ca. 2 cm \times 4 cm to serve as substrates for SWNT alignment, cleaned in piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 15:1$ in volume) at 120 $^\circ\text{C}$ for 30 min, rinsed with DI water for 1 h and dried at 120 $^\circ\text{C}$ for 1 h. Then the cleaned wafers were immersed into a 1 wt% ethanol solution of 3-aminopropyltriethoxysilane (APTS) (Aldrich) at room temperature for 2 h, rinsed with DI water for 30 min, followed by heating at 100 $^\circ\text{C}$ for 1 h. This surface treatment increases the affinity of SWNTs for the substrate surface, promoting their adhesion after they are patterned onto it.

2.4. Alignment of SWNTs on silicon substrate

PDMS microchannels were placed, channel side down, in conformal contact on the surface of a SiO_2/Si substrate. A drop (1 μl) of freshly prepared SWNT suspension was placed on the substrate near to the wide mouth of the funnel-shaped microchannel entrances. A jet of N_2 gas was directed at the droplet, with the gas blow parallel to the microchannel orientation, to push the droplet into contact with the PDMS. At contact, the droplet wetted the PDMS and was spontaneously drawn into the channels by capillary attraction. Thirty minutes after the channel filling, the PDMS microchannels were carefully removed from the silicon substrate. The N_2 gas jet was again directed at the patterned substrate, with the gas blow parallel to the deposited SWNT patterns. After the second gas flow alignment, the SWNT-patterned substrate was dried in air at room temperature, then rinsed with DI water and dried again. A schematic outline of the PDMS mold geometry and SWNT alignment procedure is shown in figure 1.

2.5. Aligned SWNTs transferred to Au/ SiO_2 electrodes

For transfer to the Au electrode, SWNTs were aligned onto a soft and flat polydimethylsiloxane (PDMS) substrate (i.e. the Si substrate in figure 1 was replaced with a PDMS substrate). The surface of the flat PDMS substrate was pretreated in argon plasma with 350 sccm Ar flow rate for 2 min in a March PX-500TM Cleaning System (March Plasma Systems, Concord, CA) operated at a radio frequency (RF) of 13.56 MHz and 100 W. The SWNTs were aligned on the surface of the flat PDMS stamp in a manner identical to that described in section 2.4. A gold electrode pair on a SiO_2/Si substrate, previously treated with $\text{HS}-(\text{CH}_2)_{11}-\text{NH}_2$

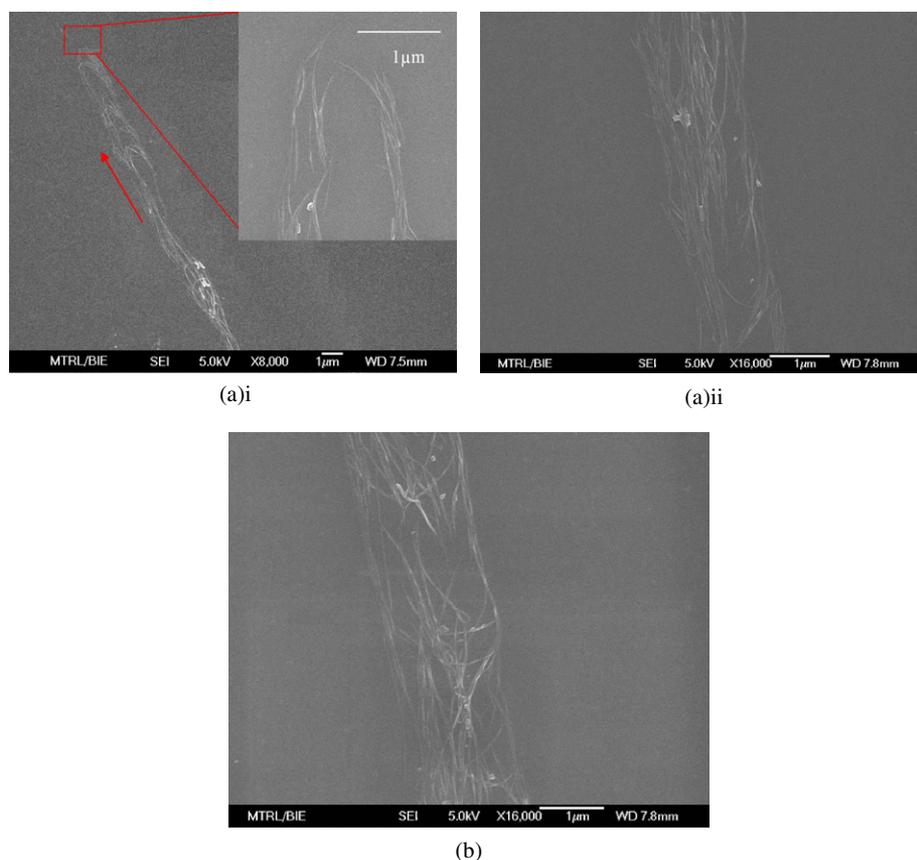


Figure 3. FESEM images of aligned SWNT pattern with (a) funnel-shaped PDMS channels and one time gas blow. (i) End of the pattern (the inset shows a magnified image of the SWNT pattern. The arrow indicates the SWNT alignment direction). (ii) Middle of pattern and (b) constant-width ($1\ \mu\text{m}$) PDMS channels. ((a)ii is apparently better aligned than (b)).

(11-amino-1-mercaptoundecane) solution, was immersed into deionized water ($\text{pH} = 4.5$) and then spin-dried (2000 rpm and 10 s) to leave a thin film of water. Then the PDMS substrate with pre-aligned SWNTs was contacted with the gold electrodes for several seconds, and then removed, transferring the aligned SWNTs to the electrodes surface.

2.6. Characterization

Optical micrographs were obtained with a Carl Zeiss Axioskop 2 MAT microscope. The SWNT pattern on the substrate was imaged with a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM). The CNTFETs were characterized at room temperature with a HP-4156B semiconductor analyzer.

3. Results and discussion

Our GAMA method to produce aligned SWNT nanopatterns involves a first gas blow for pre-alignment, flow inside microchannels for alignment and a second gas blow to draw out the aligned SWNTs into narrower patterns.

To promote pre-alignment of the SWNTs before they are initially drawn into the wide end of the funnel, the SWNT suspension droplet is placed some distance (about 5 mm) from the funnel and is blown into the entrance (figure 1(a)). The

first (i.e. pre-capillary) gas blow over the SWNT suspension droplet sets up a circulation pattern in the droplet as it is driven across the substrate toward the PDMS channeled mold. The SWNTs float in this circulation pattern and align parallel to the fluid flow to reduce resistance [42]. The SWNTs are thus somewhat aligned parallel to the channel orientation before they reach the microfluidic pattern, reducing the probability of jamming. Before the droplet dries, the SWNTs will not precipitate and deposit on the substrate surface. The wideness of the mouth of the microfluidic funnel further reduces the risk of 'log-jam' when the droplet contacts it and wets it. The fluid flow within the funnel maintains SWNT alignment as they are drawn deeper into the funnel so that they are able to be drawn by capillary action toward the narrowest point (200 nm) of the channel without jamming it. It is further apparent that this constricting flow process tends to promote aggregation of the parallel nanotubes into aligned bundles. The SWNTs are not drawn into the narrowest part of the capillary channel (a long constant-width 200 nm channel), but stop, presumably due to a partial 'log-jam' when the funnel has constricted to a width of about $1\ \mu\text{m}$.

Figure 3(a)i shows the end of the SWNT pattern after the dual alignment (i.e. first gas blow pre-alignment and funnel-shaped capillary channel) and it is still about $1\ \mu\text{m}$ wide. The funnel-shaped channels and pre-capillary gas blow permit the alignment of SWNTs in the narrower ($1\text{--}2\ \mu\text{m}$ wide) part of the microchannel but do not assist the entering of

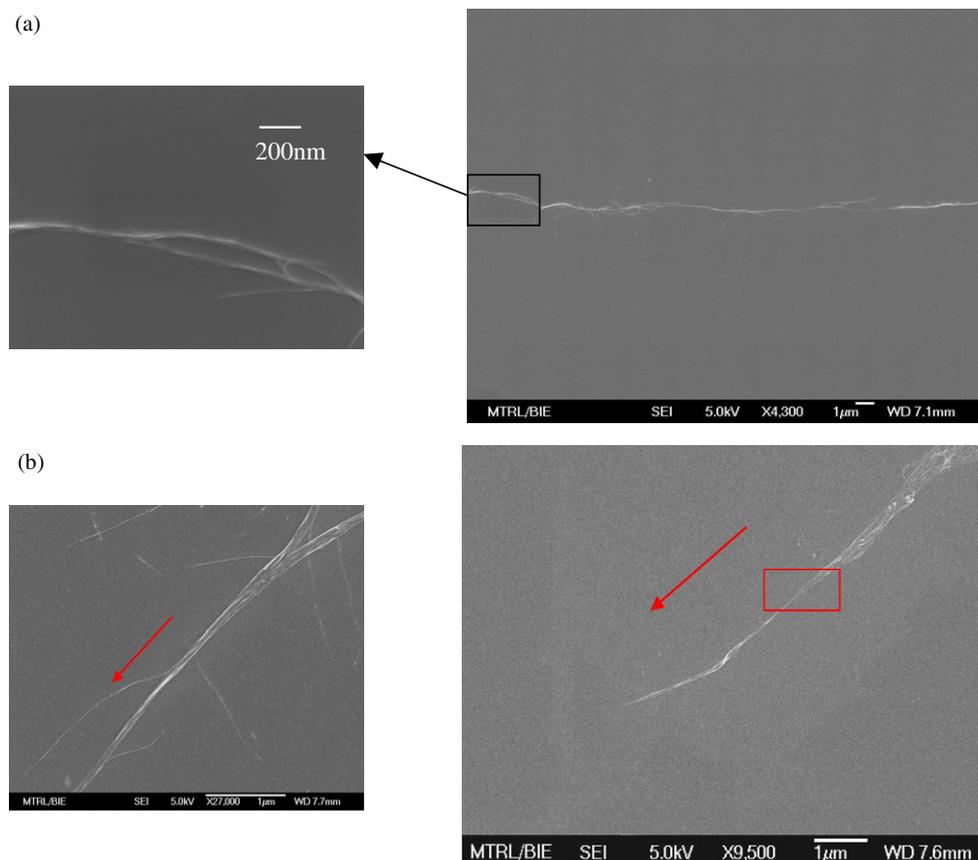


Figure 4. FESEM images of aligned SWNTs after second-time gas blow of (a) 5 s. Inset: magnified region showing nanoscale SWNT configuration. (b) 2 s. Right: a wide area of aligned SWNT pattern. Inset (left): high magnification image of aligned SWNT pattern which shows some separate SWNTs unattached to aligned SWNT bundles. Arrows show the gas blow direction. Gas pressure of 10 psi was employed.

SWNTs into the narrowest (200 nm wide) part of the channel. However, the dual alignments improve the alignment of the long (2–4 μm) SWNTs in the 1 μm -wide regions of the tapered microchannels compared to the straight 1 μm -wide channels (compare figures 3(a)ii and (b)).

To get nanoscale wide aligned patterns, we apply a second gas blow after the PDMS channeled mold is removed. From figure 4(a), after 5 s of the second gas blow, the length of aligned SWNT patterns on SiO_2/Si substrate can reach over 20 μm and the width of these patterns can be as small as 20–200 nm, i.e. significantly smaller than that achievable with simply fluidic alignment alone [33–35, 43]. At this point in the process, the substrate is not dried totally, but is covered with a thin water film. SWNTs can move along the surface of the substrate under the gas blow force, but cannot flow freely as in a droplet. The second (i.e. post-capillary) gas blow may exert a shear force on the individual SWNTs and lead to their alignment and straightening along the flow direction. When a misaligned nanotube is partly anchored to other aligned SWNTs by van der Waals interaction, the shear force would bend or rotate the tube into better alignment with longer second gas blow. In figure 4(b), when a shorter (2 s) second gas blow was applied, individual tubes that were misaligned over substantial portions of their length could be seen. The alignment becomes much better as blowing process proceeds to 5 s, as in figure 4(a). The improved alignment

with the post-capillary gas flow is due to a ‘gas spinning’ effect that resembles the ancient ‘spinning’ method for forming long connected strands from short fibers. In the second gas blow, SWNTs are carried away from the 1 μm wide pattern either by direct gas force on the SWNTs or by advection in fluid motion produced by the gas blow. As they are drawn away from the patterns, they contact other SWNTs and adhere to them, forming a connected chain. As this process continues, a continuous SWNT strand much longer than the individual SWNTs is formed.

The SWNT patterns produced by GAMA method were found to be cleaner, in the sense of having less of the usual synthetic debris, than the samples prepared by the fluidic alignment method without the gas blowings. The aligned CNTs that deposit on the substrate have an attraction to the substrate due to the attraction between the amine groups of the silane on the substrate surface and the carboxyl groups on the SWNT sidewalls [44]; the debris may have a weaker affinity for the surface and may be removed by the second gas blow. Unlike the simple one-time gas blow technique reported by others [25, 39], the pitch of our SWNT pattern is controllable by the pitch of the channels in the PDMS mold and a smaller pitch can be realized using electron beam lithography.

Figure 5 shows the results of aligned SWNTs transferred onto a gold electrode-patterned surface. The printed aligned SWNT pattern retains its orientation achieved with the

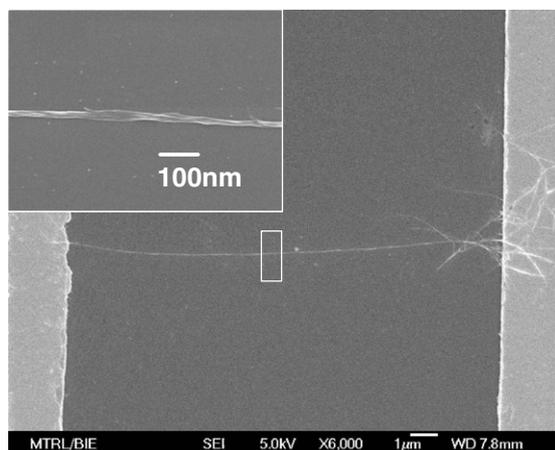


Figure 5. FESEM image of aligned SWNTs transferred to the electrode surface. Inset is the higher magnification image.

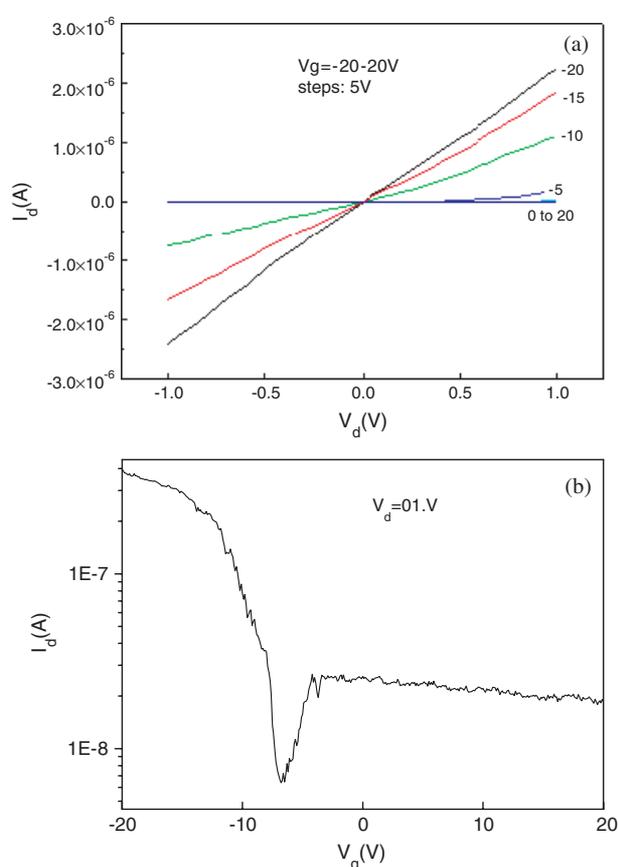


Figure 6. I_d – V_{ds} (a) and I_d – V_g curves (b) for SWNTs across two Au electrodes after annealing. The nanotubes exhibit semiconducting behavior.

gas blow alignments. The modified gold electrode surface consisted of a self-assembled monolayer of a long-chain thiol. This surface preparation was necessary for fast and clean transfer of the SWNTs from the PDMS surface to the Au electrodes. In the thin water film, the cationic $-\text{NH}_3^+$ group on gold and anionic $-\text{COO}^-$ group on SWNT complex electrostatically to transfer the SWNTs aligned on the stamp

onto the patterned gold electrode surfaces. The nanoscale aligned SWNTs bundle (about 20 nm wide) perpendicularly bridges the 15 μm electrode gap.

To reduce the contact resistance, thermal annealing at 300 $^\circ\text{C}$ for 30 min in an air environment was performed in a HP-4156B semiconductor analyzer probe station. This is expected to remove adsorbed molecules affecting the SWNT–electrode interface. Measurement of the current versus voltage of the device (figure 6) exhibits a decrease of drain current I_d with increasing gate voltage V_g over the range -20 to $+20$ V. This indicates a p-type characteristic with an ON/OFF ratio of about 10^2 ; the low ratio suggests the presence of metallic nanotubes. The resistance was about 412 k Ω , which can be mostly attributed to contact resistance between the SWNTs and the Au electrodes. These measurement results agree with previously published results [45–47].

4. Conclusions

We present a simple but effective microfluidic method employing a funnel-shaped capillary alignment channel combined with pre- and post-capillary gas blow alignments; this enables facile fabrication of aligned SWNT patterns with nanoscale width, micron-scale lengths and controllable pitch. SWNT patterns with widths as narrow as 20 nm but lengths of up to 15 μm have been demonstrated. With suitable adjustment of the process parameters, the length and width of aligned SWNTs can be controlled as needed for specific nanodevices. The CNTFETs fabricated with SWNTs using this technique show p-type characteristics.

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