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Alignment of Nanoscale Single-Walled Carbon Nanotubes Strands

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Abstract: Depositing single-walled carbon nanotubes (SWNTs) with controllable density, pattern and orientation on electrodes presents a challenge in today's research. Here, we report a novel solvent evaporation method to align SWNTs in patterns having nanoscale width and micronscale length. SWNTs suspension has been introduced dropwise onto photoresist resin microchannels; and the capillary force can stretch and align SWNTs into strands with nanoscale width in the microchannels. Then these narrow and long aligned SWNTs patterns were successfully transferred to a pair of gold electrodes with different gaps to fabricate carbon nanotube field-effect transistor (CNTFET). Moreover, the electrical performance of the CNTFET show that the SWNTs strands can bridge different gaps and fabricate good electrical performance CNTFET with ON/OFF ratio around 10^6. This result suggests a promising and simple strategy for assembling well-aligned SWNTs into CNTFET device with good electrical performance.

Keywords: Single-walled carbon nanotubes; Microchannel; Capillary force; Carbon nanotube field effect transistor

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Introduction

SWNTs have experienced rapid research and development since they were produced independently by Iijima and Bethune in 1993 [1,2]. SWNTs have drawn much attention not only for their superior electronic mobility, but also for their nano-scale diameter, unique physical properties, and semiconducting behaviour [3,4]. Nowadays, SWNTs are considered as a promising building block in the future silicon-based electronic technology. For example, in the integrated circuit field, these materials have been achieved to scale the metal oxide field-effect transistor (FET) into smaller dimension [5,6]. More importantly, the small diameter and long length of SWNTs can be used to fabricate CNTFET to replace silicon in nanoelectronic devices, where silicon and other standard semiconductors can not work in a molecular scale.

As-produced SWNTs are highly entangled, and the diameter of the nanotubes bundles is always tens of nanometers, which might limit their real applications. In practical application, nanotube-based devices, such as FET, use carbon nanotubes between two metal electrodes as an electrons flowing channel. Hence, how to deposit the SWNTs pattern with controllable density, orientation and narrow width on electrodes to get a device with good electrical property is still a key challenge for the electrical engineers. Some scientists have successfully used the atomic force microscope (AFM) tips to locate single carbon nanotube between the sources and drains [7]. However, it is difficult to manipulate many nanotubes extensively in real applications.

According to many recent publications, there are two important methods to align SWNTs: (1) in situ synthesis and (2) post synthesis ordering [8]. The first approach includes chemical vapour deposition (CVD)

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processes on a pre-patterned (with catalyst) surfaces or a template-based synthesis. However, this method requires high temperature (>800℃) and a reactive environment which would influence the stability of devices, so as to limit its application [9,10]. Furthermore, this method will also introduce many metallic catalysts which are difficult to remove, so as to affect the electric properties of fabricated devices. As for the second method, a few publications have been reported over the past few years including fluidic flow-directed assembly method [11,12] and Langmuir-Blodgett (LB) assembly method [13]. Besides, electric-field or magnetic-field has been also developed to control nanotubes in patterns [14,15]. Although some of these methods can align the carbon nanotubes in large scale area with micro-scale width, it is obviously difficult to fabricate a massively parallel or complex pattern with nano-scale width at precise location when applied in real silicon-based electronic nanodevice.

In this paper, we present a new assembly technique to align SWNTs into parallel patterns with nanoscale width. The photo-resist resin microchannel template was patterned on the silicon wafer surface. The silicon substrate was treated with amine-ended saline to get a hydrophilic surface. When the dilute SWNTs suspension flow into microchannels, the capillary force can stretch and align carbon nanotubes one by one into a nanoscale strand. After removed of the photoresist resin, the aligned carbon nanotuebs was transferred to gold electrodes surface to fabricate CNTFET.

Experimental section

Preparation of SWNTs suspension

About 50 mg of pristine SWNTs (Purchased from Chengdu Organic Chemicals Co. Ltd., China) were treated in 100 ml of 2.0 mol/l HNO_3 for 4 h to introduce carboxyl groups (–COOH) on the surfaces. After that, the solid was diluted in deionized (DI) water and filtered with a PTFE filtration membrane (with an average pore diameter of 0.2 μm) repeatedly for 5∼6 times. Then, these purified SWNTs, about 2 μm long, were dispersed in an aqueous sodium dodecyl sulfonate solution (SDS 2.0 wt%). The concentration of the SWNTs in the final solution was approximate to 1.0×10^{-3} mg/ml. Before each use, the suspension was centrifuged at 10 000 rpm for 1 h and the supernatant CNT solution was collected for this experiment.

Silicon substrate with photoresist resin microchannels

Photoresist resin grooves with rectangular cross section on the surface of silicon wafer with silicon dioxide 100 nm layers were fabricated by using standard photolithographic methods. The grooves of the microchannel were separated by 1.5 μm ridges, again with rectangular cross section. The depth of the grooves was (1.0±0.5) μm, length was 900 μm, and their width was (1.0±0.5) μm. Then, the wafers were immersed into an amine-containing silane (3-aminopropyltriethoxysilane (APTES), 0.5 wt%) solution at room temperature for 4 h. After washed by DI water, the wafers were dried with nitrogen, and then underwent a thermal treatment at 100℃ for 2 h.

Alignment of SWNTs

The silicon substrate with photoresist resin microchannel pattern was put on the flat hot plate. A drop (0.2∼1.0 μl) of freshly prepared SWNTs suspension was introduced into the microchannels, and then the suspension would fill the channels via capillarity in a few minutes. After that, the suspension-filled microchannels were dried in the air at 40℃. The same procedure can be repeated several times. The surfactant was washed away by DI water, and photoresist resin was removed by acetone.

Transfer SWNTs strands onto electrodes surfaces

The electrode comprised a silicon substrate, coated with a 500 nm thickness SiO_2 layer, with a pattern of parallel gold stripes of 100 nm thickness deposited on the SiO_2. The $HS(CH_2)_{11}NH_2$ self-assembled monolayer (SAM) was prepared by immersing the electrode (previously treated in piranha solution at 90℃ for 10 min) into the HS $(CH_2)_{11}NH_2$ toluene solution (0.5 mmol/l) for 12 h. After monolayer assembly, the electrode was thoroughly rinsed with toluene and sonicated in ethanol for 15 s to remove possible surface contaminants. Then this gold electrode was immersed into HCl solution (pH=2.0) to convert the NH_2 to NH_3^+. The silicon substrate with aligned CNTs was perpendicularly contacted with the gold electrodes for 1 h at room temperature, then heat at 200℃ for 3 h, and then removed, transferring the aligned CNTs to the gold surface.

Characterization

The SWNTs pattern on the substrate was observed by a Field Emission Scanning Electron Microscopy (FE-SEM, JEOL, JSM-6700F) to evaluate the morphology of the samples. An atomic force microscope (AFM, Asylum Research, MFP-3D) has been used for surface imaging and measurements of force-distance curves in air. The CNTFETs have been characterized at room temperature using a HP-4156B semiconductor analyzer.

Results and discussion

Fluidic assembly method is one of the most effective ways to align nanowires/nanotubes in a pattern surface, and the simplest technique is through the use of an evaporating liquid droplet. Figure 1(a)-(d) shows the schematic illustration of SWNTs strands aligned on silicon substrate by the shear force of solvent evaporation method. First, we coated a layer of photoresist resin on the silicon wafer surface to fabricate photoresist resin grooves with rectangular cross section by using standard photolithographic methods. Then a drop of SWNTs suspension was dripped into microchannels, and it spread and flowed into microchannels in a few seconds. As the suspension is undergoing evaporation, the capillary force can stretch and align carbon nanotubes one by one into a nanoscale strand. Similarly, it can also be demonstrated that this fluidic assembly method is successful in achieving high-density (about 10∼20 nanotubes μm^{-1}) aligned nanotubes [16].

It is well known that when a droplet containing nanoparticles or nanotubes is dried on a flat substrate, ring-like structures are usually observed because of the migration of nanoparticles or nanotubes toward the three phase contact line at the perimeter of liquid dome [17,18]. Similarly, if the substrate is patterned into areas having different wetting (hydrophilic/hydrophobic) properties, solution containing nanowires or nanotubes will preferentially attach to predefined channels with hydrophilic properties while the hydrophobic areas have little or no affinity to the solution. After the solution is evaporated, the nanowires/nanotubes can only be confined in the hydrophilic area. Figure 1(e) shows the alignment mechanism of solvent evaporation method used in this work. As a thin liquid film attached in the hydrophilic microchannels starts to evaporate, the contact receding lines in trenches will move downward during the process, and SWNTs tend to migrate upward along the channels towards the three phase contact line. Once one end of SWNTs is pinned by van der Walls force or chemical bonding between –COOH on carbon nanotubes and $–NH_2$ on the functionalized surface of silicon dioxide, the capillary force is exerted by the contact line on nanotubes which can be stretched and aligned perpendicular to the liquid front edge. Similar mechanism has been reported to assemble high aspect ratio structures of single DNA molecules [19].

From the surface topography of SWNTs after one-time alignment (Fig. 2), we can see that most SWNTs are aligned into straight bundles lying on the middle line of microchannels (dark-colored area), and the diameter of SWNTs bundles is around tens of nanometers. Due to the different wettability, the SWNTs suspension preferred to flow on hydrophilic silicon surface in the channels bottom (light-colored area). Ultimately, most SWNTs are located in the middle of microchannels one by one, while there is no carbon nanotubes left on the photoresis resin patter surface. By controlling the wettability of substrate, we successfully aligned SWNTs at the desired location.

However, it is noticed that the SWNTs bundles are difficult to link each other into a continuous strand as shown in Fig. 2 (identified by write arrow in "(b)"). To get continuous strands, we applied a second process after the channels dried. In this procedure, we tilted the substrate with a slight degree (∼10°) to assist the

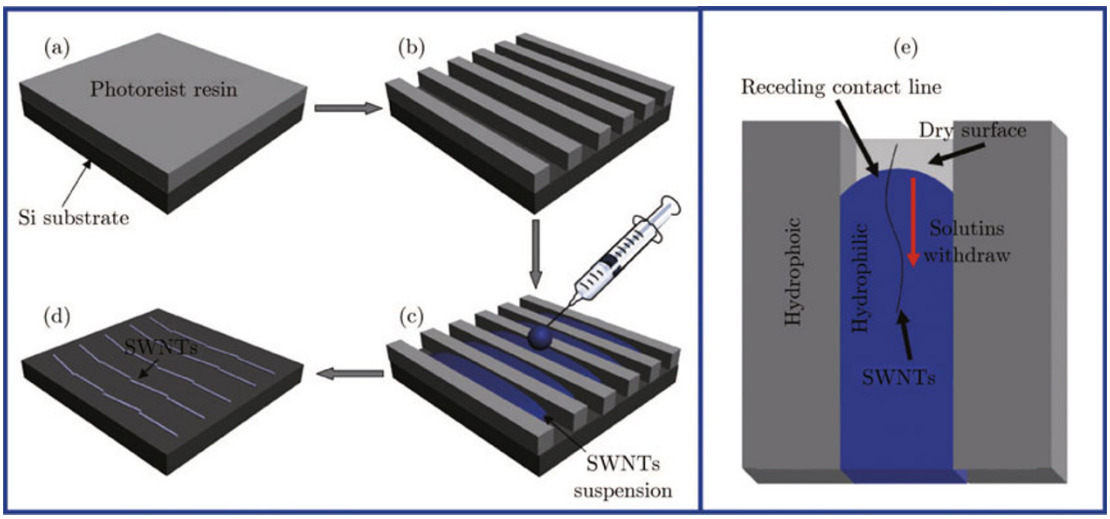

Fig. 1 Schematic illustration of SWNTs strands align on silicon substrate by the shear force of solvent evaporation(a-d): (a) a layer of photoresist resin is coating on the silicon wafer surface, and (b) photoresist resin grooves with rectangular cross section were fabricated by using standard photolithographic methods, then (c) a drop of SWNTs suspension was introduced into the microchannels. As the suspension evaporating, the capillary force can stretch and align carbon nanotubes one by one into a nanoscale strand (d). (e) Mechanism of the SWNTs strands aligning in the mirochannel.

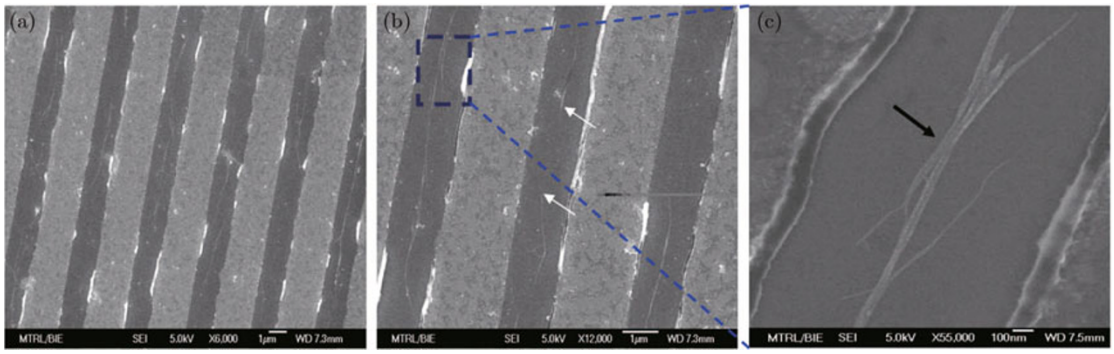

Fig. 2 FESEM images of SWNTs aligned in photoresis microchannels after one-time alignment. Some of the SWNTs are difficult to link each other into a continuous strand (identified by write arrow in "(b)"), and the others are connected one by one (identified by black arrow in "(c)"). (Magnification (a): 6 000; (b): 12 000; (c): 55 000).

alignment and avoid leaving too much SWNTs. From the FESEM images of SWNTs strands after a dual alignment (Fig. 3), we can see that continuous nanoscale diameter SWNTs strands are aligned on the substrate of microchannels uniformly. These results show many differences with the common dip-coating results reported by other papers in which the SWNTs spread on whole substrate surface or just in two corners of the microchannels layer by layer [20,21]. In our experiment, the crucial factors that can affect the result include low concentration SWNTs, uniform and straight microchannles pattern and enough gaps with different hydrophobic/hydrophilic properties between photoresit resin and substrate (the discrepancy of contact angle is larger than 80°). In the first aligning process, these factors can ensure the single nanotubes or bundles SWNTs located in the desired microchannels. In the second process, as the three phase contact line receded, the front of convex liquid deformed because the aligned SWNTs existed, which had an affinity to the suspension as the result of surface tension. As a consequence, during the second process, SWNTs in suspension one by one adhered to the aligned SWNTs produced in first process, which resulted in SWNTs strands longer and wider. In addition, we can obtain tens or hundreds of micrometer SWNTs strand according to the microchannels patter design. With one more alignment process, the SWNTs strands show wider diameter and tangled patterns with some carbon nanotubes attached to the side strands (Fig. 4). If this process continues several times, SWNTs layer will cover the entire substrate surface which is same as the common microfluidic-method result that we reported previously [20]. To get uniform nanoscale SWNTs strands, a dual alignment is necessary and the twice process may be the most suitable experimental procedure.

Figure 5 shows the AFM images of the bridged SWNTs stands with two kinds of electrodes, 8 μm and 16 μm gap, respectively. Before the transfer of the aligned SWNTs strand to patterned gold electrodes, the Au surface was treated by amine-ended thiol to get cationic $-NH_3^+$. During wet contact printing, the anionic $-COO^-$ group on SWNTs formed a chemical bond with $-NH_3^+$ on Au surface. From AFM images (Fig. 5(a) and 5(c)), we can see that the SWNTs strands is aligned on electrode surface successfully and the diameter is about 30 nm. And by this method we can also prepare enough long SWNTs strands to bridge any electrodes with short or wide gap. What's more, it may provide an approach to fabricate controllable aligned SWNTs strands on gold electrodes and explore more applications.

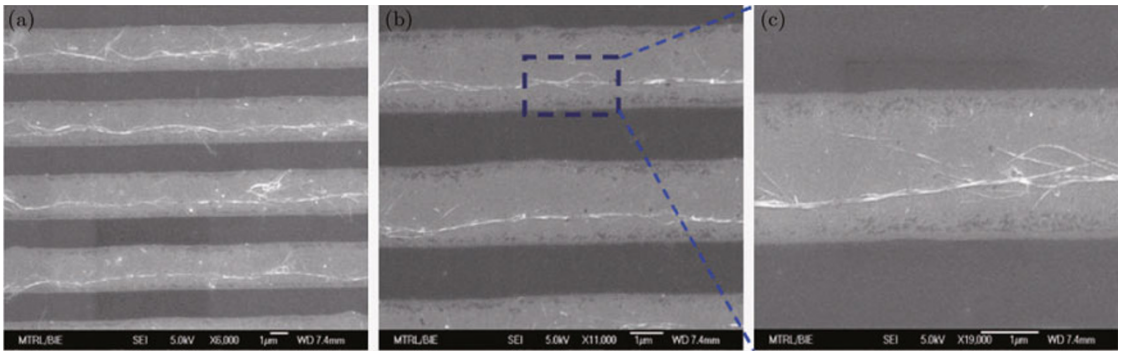

Fig. 3 FESEM images of SWNTs strands on substrate with twice process after remove of photoresist resin. Continuous nanoscale diameter SWNTs strands are aligned on the substrate of microchannels uniformly and each SWNT is connected to other end to end. (Magnification (a): 6 000; (b): 11 000; (c): 19 000)

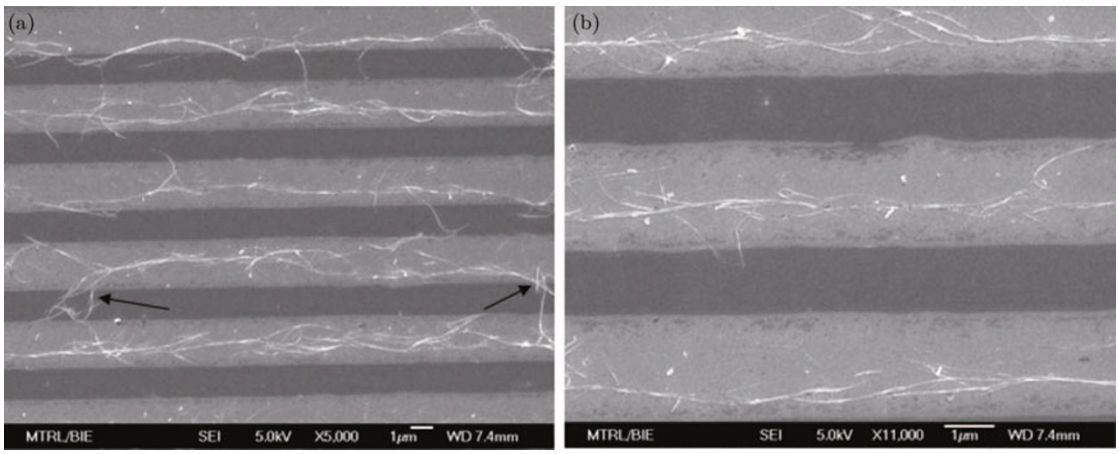

Fig. 4 FESEM images of SWNTs strands on substrate with thrice process after remove of photoresist patterns. The SWNTs strands show wider diameter and tangled patterns with some nanotubes attached to the side strands (identified by blank arrow in "(a)"). (Magnification (a): 5 000; (b): 11 000)

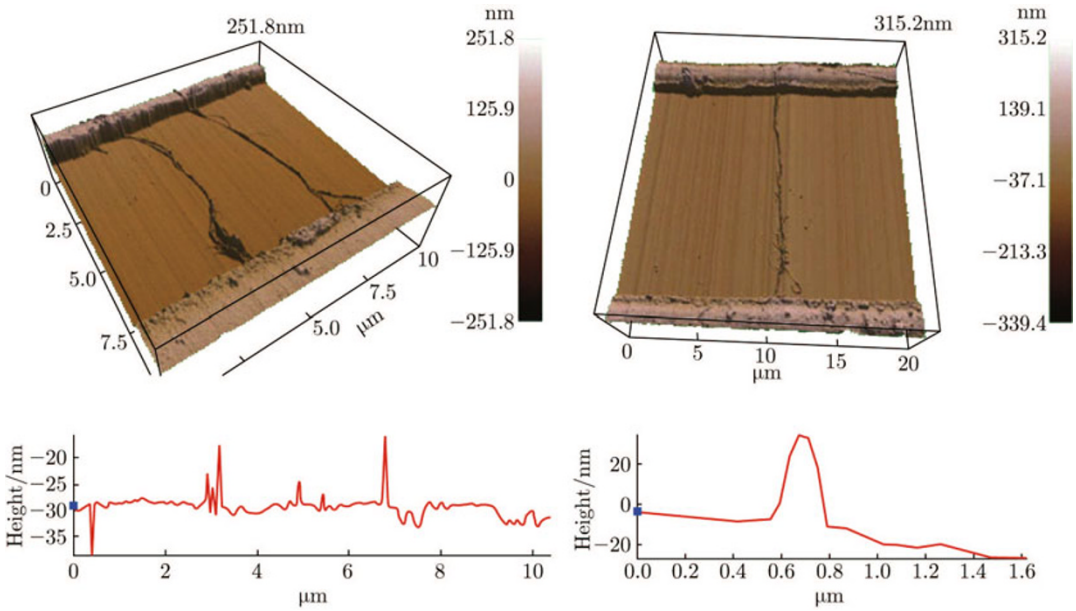

Fig. 5 AFM images ((a), (c)) and the height-distance curves ((b), (d)) of SWNTs strands on the pattern electrodes ((a), (b): 8 μm gap; (c), (d): 16 μm gap).

To reduce the contact resistance, a thermal annealing procedure was performed in the HP-4156B semiconductor analyzer probe station at 300℃ for 30 min in the air environment. This is expected to remove adsorbed molecules affecting the tube-electrode interface. From the output characteristics of the CNTFET device (Fig. 6), we can see that the drain current I_d decreases with increasing gate voltage V_g in the range between −10 V and +10 V. Our SWNTs demonstrate the characteristic field effect p-type transistor (FET) behaviour. And the resistance was 357 kΩ, which can be mostly attributed to the contact resistance between SWNT and Au electrodes. The ON/OFF ratio is around 10^6. These measurements, as show in Fig. 6, are also similar to previously published nanotubes conductivity test results (deposited by other methods) [22,23].

The results achieved by solvent evaporation method in our experiment may provide an approach to study and construct complex SWNTs architectures, and explore more potential applications such as active elements in transistors, horizontal interconnect systems and sensors [24-27].

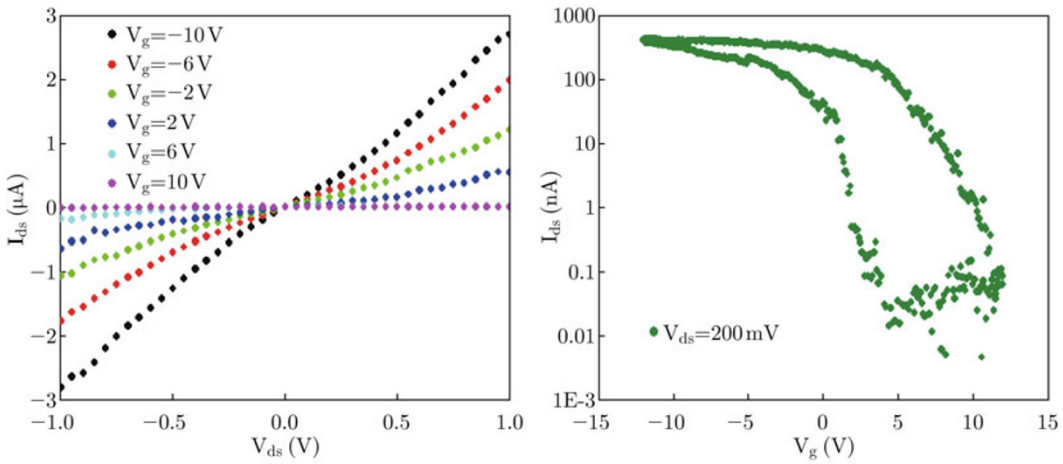

Fig. 6 I-V (a) and I_d-V_g curves (b) of the CNTFET device fabricated with aligned SWNTs across two Au electrodes separated by 16 μm gap. These SWNTs show a characteristic field effect p-type transistor behaviour.

Conclusions

We have assembled SWNTs into uniform nanoscale diameter strands patterns using a simple microfluidic technique. By controlling hydrophilic/hydrophobic properties of photoresist resin pattern and silicon oxide substrate, we successfully obtained align SWNTs strands with desired diameter and length after processed twice. This method provides a simple and effective way to build organized SWNTs strands pattern in large scale. After the transfer to Au electrodes surfaces, the SWNTs strands can bridge different gaps to fabricate CNTFETs with good performance. We also think this technique has immense implications for the development of carbon nanotubes based electrical nanodevice.

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