



# Aligned, Ultralong Single-Walled Carbon Nanotubes: From Synthesis, Sorting, to Electronic Devices

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Aligned, ultralong single-walled carbon nanotubes (SWNTs) represent attractive building blocks for nanoelectronics. The structural uniformity along their tube axis and well-ordered two-dimensional architectures on wafer surfaces may provide a straightforward platform for fabricating high-performance SWNT-based integrated circuits. On the way towards future nanoelectronic devices, many challenges for such a specific system also exist. This Review summarizes the recent advances in the synthesis, identification and sorting, transfer printing and manipulation, device fabrication and integration of aligned, ultralong SWNTs in detail together with discussion on their major challenges and opportunities for their practical application.

### 1. Introduction

Single-walled carbon nanotubes (SWNTs) have attracted widespread attention since their discovery in 1993 because of their unique structural, electrical, optical, chemical, thermal, and mechanical properties. [1-6] The promising applications of SWNTs in future nanoelectronics has motivated intense research in various aspects from synthesis, properties, to electronic devices. Individual SWNT field-effect transistors (FETs) have demonstrated excellent performance over current silicon-based complementary metal oxide semiconductor (CMOS) devices.<sup>[7]</sup> Although the performance of individual SWNT FETs has been pushed nearly to its theoretical limit, [8,9] there are still great challenges for their practical application in electronics as a result of the lack of an effective integration strategy. Obviously, the first step towards integration is to get well-ordered SWNTs on the wafer surface. Two approaches have been used to produce aligned SWNTs: assembly and growth. The assembly techniques utilize either specific tube-substrate interactions or external fields, such as electric field, to achieve a controlled deposition of SWNTs from solution onto patterned surfaces. [10–18] These approaches involve dispersion of SWNTs into a liquid medium and are, therefore, limited to short and chemically functionalized tubes ( $<1 \mu m$ ). Moreover, it is hard to control the exact location and packing density of nanotubes on wafer surfaces via assembly. Directly controlled growth by chemical vapor deposition (CVD) provides a more promising way for getting aligned SWNTs on the wafer surface. Liu and his colleagues pioneered the synthesis of well-aligned SWNT arrays on a surface by the fast-heating technique. $^{[19-21]}$  Up to now, a number of approaches have been developed to produce high-quality, well-aligned SWNTs by introducing aligning forces during the growth

process, such as gas flow,<sup>[22–26]</sup> external field,<sup>[27–30]</sup> and surface lattice.<sup>[31–34]</sup> The lengths of SWNTs can reach up to the wafer scale.

The aligned, ultralong SWNTs represent attractive building blocks for nanoelectronics because of the following features: First, the quality of thus-grown SWNTs is very high. The intensity ratio of D band and G band  $(I_D/I_G)$  of such ultralong SWNTs is very low, [24,25,35,36] which indicates an extremely low density of defects in the tube structures. Electrical measurements reveal that the outstanding electrical properties of these SWNTs can be extended to centimeter scale. The resistance per unit length is  $\sim$ 7 k $\Omega$   $\mu$ m<sup>-1</sup> and the mean free path of electrons is  $\sim$ 1  $\mu$ m; values which are comparable to the best short SWNTs to date. [37] Second, the structures and electronic properties are uniform along individual tubes. Raman study along one single tube axis revealed that most tubes exhibit a uniform radial breathing mode (RBM) spectrum over a centimeter length scale. [24,25,35] Therefore, all electronic devices made from the individual tubes have exactly the same performance. Third, the ultralong length of SWNTs allows for fabrication of a large number of devices on an individual tube. Avouris and co-workers have fabricated a five-stage ring oscillator based on a single 18 µm long tube, [38] beautifully demonstrating the possibility of creating integrated circuits on individual carbon nanotubes. Fourth, the nanotubes are well-organized in two dimensions (2D) on the wafer surface, either parallel or even crossbar, thus, facilitating the large scale integration of unit devices.

Despite the above advantages, great challenges for such CVD-grown, aligned, ultralong SWNTs also exist on the way to future nanoelectronic integrated devices. First of all, although a few approaches have shown some promise in chirality control, [39-43] it is still difficult to get single chirality or even

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pure semiconducting/metallic tubes. Obviously, it is not a good choice to disperse or dissolve the well-aligned SWNTs system nanotubes in a liquid medium for the purpose of chiral or semiconducting/metallic separation. Furthermore, the high-temperature CVD process for growing aligned, ultralong SWNTs is not compatible with most substrates, especially plastics and chips that contain prepatterned electrodes and circuits. This means that one needs to develop a suitable transfer-printing technique to transplant the SWNTs array from their growth substrates to other substrates that have designed structures or a chemical nature.

In this Review, we present the recent progress on ultralong SWNT studies from the viewpoint of nanoelectronic integrated devices. The second section summarizes synthesis methods of aligned ultralong SWNTs. The following two sections focus on the approaches to solving the problems for nanoelectronic applications mentioned above (i.e., sorting/separation and transplantation of ultralong SWNTs on surfaces). Methods which are developed for short and random tubes but can be extended to ultralong surface tubes are also included. The fifth section describes various electronic devices and circuits made from ultralong SWNTs. Finally, we conclude with some perspectives on opportunities for future work.

### 2. Synthesis of Aligned, Ultralong SWNTs

The key to growing aligned, ultralong SWNTs on a substrate surface is to apply a suitable aligning force to direct the growth of the nanotubes during CVD growth. A number of methods have been developed for growing parallel, ultralong SWNTs using various aligning forces, including electric-field-directed growth, gas-flow-directed growth, and lattice- or step-oriented growth. In this section, we will discuss the key technical points, mechanisms, advantages, and limitations of these methods. Direct CVD growth of complex SWNTs architectures such as crossbar and serpentine tubes by the combination of gas-flow-directed growth and lattice-oriented growth, local diameter modulation of ultralong SWNTs by temperature-oscillation growth, and chirality control of SWNTs by cloning growth via an open-end growth mechanism will also be shown.

### 2.1. Electric-Field-Directed Growth of SWNTs

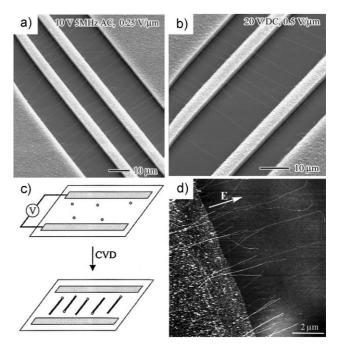
Dai and co-workers applied an external electric field to direct the growth of suspended SWNTs on prepatterned quartz substrate,  $^{[44]}$  where poly-silicon was used as the electrode material. Figure 1a and b exhibits the suspended SWNTs array grown at different electric fields. The optimum field strengths for directed growth of suspended SWNTs were in the range of 0.5–2 V  $\mu m^{-1}$ . The field-alignment effect here originates from the high polarizability of SWNTs. In subsequent work,  $^{[29]}$  they succeeded in growing aligned SWNTs on thermally grown  $SiO_2/Si$  substrates using Mo as electrodes. The authors calculated the electric-field distribution at a bias voltage of 10 V and pointed out that the carbon nanotubes were aligned up along electric field lines during CVD growth. A similar electric-field-aligning strategy was employed by Lieber



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and co-workers.<sup>[30]</sup> They believed that when SWNTs grew under an electric field, as shown in Figure 1c, a dipole would be induced in the SWNTs. The large induced dipole moments led to remarkable aligning torques and forces on the nanotubes, which prevented the randomization of nanotube orientation (Fig. 1d). Obviously, the tube length grown by electric-field-directed CVD growth is restricted by the separation distance of electrode pairs. The lithographic process for fabricating electrode pairs also makes this approach complicated and time-consuming.



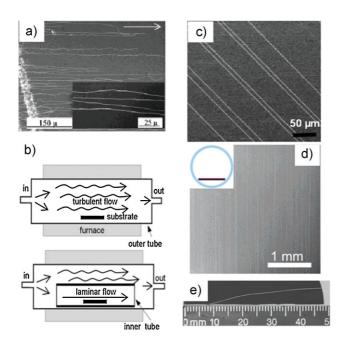
**Figure 1.** Electric-field-directed growth. a,b) Scanning electron microscopy (SEM) images of suspended SWNTs grown at different electric fields. The nanotubes show clear alignment in the electric-field direction. Reproduced with permission from [44]. Copyright 2001, American Institute of Physics. c) Schematic representation of vectorial growth of SWNTs. d) Atomic force microscopy (AFM) image showing electric-field-directed growth of long SWNTs on oxidized silicon wafers. Reproduced with permission from [30]. Copyright 2002, American Chemical Society.

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#### 2.2. Gas-Flow-Directed Growth of SWNTs

Gas flow was found to be an effective aligning force to guide the growth direction of SWNTs. Most of the recent work on the synthesis of arrays of ultralong SWNTs are based on this approach. The gas-flow-directed growth method was first reported by Liu and co-workers. [19,21,22] Without using a strong electric field during CVD growth, Liu and colleagues achieved an array of horizontally aligned, millimeter-long SWNTs on flat substrates, as shown in Figure 2a. [19] The use of a fast-heating treatment at the initial stage of growth is the major difference from the conventional CVD method, which produces random and short carbon nanotubes. The key to the fast-heating treatment is to rapidly transfer the catalyst-loaded substrate into the preheated center zone of the CVD furnace. The sudden exposure of the growth substrate to a 900 °C environment induces convection flow because the substrate and its surrounding gas molecules are heated up at different speeds and thus have different temperatures at the initial fast-heating stage. This convection flow would help to lift up the catalyst nanoparticles together with the growing nanotubes. The floating carbon nanotubes are then aligned by gas flow in the growth process. With an optimized growth condition, the tube length can be up to centimeters long with this fast-heating technique, though the growth density is relatively low. Nevertheless, this technique did



**Figure 2.** Gas-flow-directed growth. a) SEM images of a horizontally aligned SWNT array grown from the fast-heating CVD process. Reproduced with permission from [19]. Copyright 2004, American Chemical Society. b) Schematic illustration of tube-in-tube setup for generating laminar flow. c) SEM image of aligned SWNTs grown in the laminar flow system. Reproduced with permission from [48]. Copyright 2005, American Chemical Society. d) SEM image of an array of aligned SWNTs by ultralow feeding gas CVD. Reproduced with permission from [26]. Copyright 2007, American Chemical Society. e) Photograph of a 4.8 cm long SWNT grown by ethanol. Reproduced with permission from [49]. Copyright 2004, Nature Publishing Group.

not find widespread application by other researchers because the experimental operation is not easy for achieving fast heating with safety. Moreover, it seems difficult to obtain a perfectly aligned array of SWNTs in such a way. In the subsequent work, [45] Liu and co-workers developed an in situ catalyst-floating technique for growing long and well-oriented SWNTs on substrates. They utilized CO as the carbon source and Fe powder as the catalyst. In a specifically designed two-furnace system, CO was reacted with Fe powder, forming iron carbonyl in the first furnace. The intermediate iron carbonyl was brought into the second, high-temperature furnace by gas stream and decomposed into floating Fe catalyst nanoparticles. As a result, gas-flow-aligned, long SWNT arrays were obtained on the underlying substrate surface. [45]

Apparently, the key for the gas-flow-directed growth of SWNTs is to create an experimental condition that allows catalytic nanoparticles and hence the growing nanotubes to float up into the gas phase from the substrate surface. The floating tubes, which are not influenced by van der Waals dragging of the substrate, keep growing longer and are then aligned by gas flow. Such a floating growth mode can effectively avoid the surface-induced catalyst poisoning as compared with the surface growth mode. This would explain why ultralong, aligned SWNT arrays can be grown by the gas-flow-directed CVD technique. Direct evidence of the floating growth comes from the fact that the grown SWNT arrays can cross over trenches and vertical barriers on the substrate surface. [19,46] Kong and co-workers designed an in situ sample-rotation setup to confirm how the carbon nanotubes are floating, partially or totally, over the substrate surface. [23] They found that together with the change of the angle between the nanotubes and substrate (to which the settled nanotubes are attached) and the gas flow direction that aligns the floating nanotubes (0°, 30°,  $-30^{\circ}$ ), the surface orientation of aligned SWNTs completely changed accordingly. This suggests that the long carbon nanotubes are completely floating over the substrate surface during growth. The settling process, that is, the sinking of a floating tube to the substrate surface, might result from thermal vibration or flow-induced fluttering. A higher order of oscillation would bring the upstream part of the nanotubes in touch with the substrate surface, leading to the settling of floating tubes. They believe that the settling process is stochastic because the settling rate was constant over time. Further atomic force microscopy (AFM) studies indicate that both tip and base growth mechanisms are fitting for the growth of aligned long SWNTs.[47]

The flowing dynamics of feeding gas plays an important role in controlling the alignment and growth length of SWNTs. A stable laminar flow of feeding gas was found to facilitate the directional growth of SWNTs with long-distance traveling. As demonstrated by Kim et al., by adjusting the Reynolds number of gas flow used in a tube-in-tube geometry (Fig. 2b), well-aligned and ultralong CNTs have been grown with methane at 950 °C (Fig. 2c). The tube length was up to  $\sim\!10\,\mathrm{cm}$ , which was only limited by substrate size and furnace design. In fact, it is not necessary to use a high gas flow rate for guiding the growth direction of SWNTs. In subsequent work by Li and co-workers,  $^{[26]}$  an array of well-aligned SWNTs was grown with an extremely low gas flow rate, 1.5 sccm in a 1 inch quartz tube reactor. The typical result with CH<sub>4</sub> and H<sub>2</sub> at 970 °C is shown in Figure 2d. The buoyant

force arising from gas temperature and hence density difference is believed to contribute to the tube alignment together with the laminar flow.[23,26]

The carbon source is also one of the critical issues for achieving aligned SWNTs on a substrate surface. Using ethanol as the source material, Zhu and co-workers obtained 4 cm long SWNTs at a growth temperature of 900 °C without using the specific fast-heating treatment (Fig. 2e). [49] They believed that the tube length was only limited by the dimension of the substrate used. The heating speed showed a minor effect on the length and density of SWNTs. Almost at the same time, O'Brien and co-workers succeeded in growing ultralong SWNT arrays using ethanol as carbon source and bimetallic CoMo-doped mesoporous silica as catalyst. [46] Dispersion of the catalyst into the mesoporous silica host was expected to effectively prevent catalytic nanoparticles from aggregating at high growth temperatures. In this case, a base growth mechanism would better explain the obtained results because the catalysts were embedded in the mesoporous silica host. [46] A trace amount of water (0.2-5 wt%) contained in ethanol was found to greatly facilitate the growth of oriented SWNTs. [50] Thus-grown SWNTs could traverse slits as wide as hundreds of micrometers and fly over vertical barriers as high as 20 µm. Water in the ethanol might act as a mild oxidizer to clean the carbon nanotubes and catalytic Co nanoparticles. Such a self-cleaning process would elongate the lifetime of catalysts, leading to the growth of ultralong SWNT arrays until the Co nanoparticles lose activity or drop down to the substrate surface. It is believed that ethanol is a unique carbon source suitable for growing ultralong SWNTs, originating from its high reactivity and dissociation property. The high reactivity of ethanol molecules at growth temperature would result in a fast growth rate of SWNTs. As measured by Zhu and co-workers, the growth rate of SWNTs using ethanol was as high as 11 µm s<sup>-1</sup>. [49] On the other hand, the dissociation of ethanol molecules does not tend to form amorphous carbon. These specific features of ethanol would greatly facilitate the efficient growth and alignment of ultralong SWNTs.

The catalyst is an important factor affecting the growth of SWNTs. In addition to the widely used Fe, Co, Ni, and Co-Mo, Cu and Pb are also found to work as effective catalysts for the high-efficiency growth of ultralong, aligned SWNT arrays on surfaces. [51] Li and co-workers first demonstrated the catalytic effect of Cu on growing a high-density array of horizontally aligned SWNTs using methane, ethanol, and 2-propanol as carbon sources on a SiO<sub>2</sub>/Si substrate. [51,52] The packing density of SWNTs was as high as 2-3 tubes/10 μm. Molecular dynamics calculations indicated that the interaction between Cu and SiO2 is much lower than Fe and SiO2. This, together with the high vapor pressure of Cu, would favor the floating growth mode, consistent with the experimental observation that the directional growth of ultralong SWNTs was independent of the use of fast-heating treatment. Similar results have been obtained with Pb catalysts by the same group though an excess loss of high-vapor pressure Pb was unavoidable during the CVD process.<sup>[52]</sup> Considering the non-ferromagnetic property and easy removal of low melting and boiling point Cu and Pb, use of these catalysts provides an attractive way to investigate the intrinsic magnetic properties of SWNTs. Surprising progress on the exploration of growth catalysts of SWNTs was achieved by Huang and his colleagues

recently. They found that nanometer-sized SiO2, Al2O3, TiO2, and lanthanide oxides, except promethium oxide, can also work as catalysts for growing aligned long SWNTs. [53] Furthermore, by applying the fast-heating technique or using ethanol as the carbon source, they even succeeded in growing aligned SWNT arrays on quartz and Si substrates without using any catalysts.<sup>[53]</sup> These findings suggest that there is much more space for improvement and exploration of the catalyst design of SWNT growth. On the other hand, more efforts are needed to fully understand the catalytic growth mechanism of ultralong SWNTs.

### 2.3. Lattice- or Step-Oriented Growth of SWNTs

Alignment of SWNTs can be induced by growing on some crystalline substrate surfaces such as sapphire and quartz;<sup>[31–33,54–57]</sup> this has become the most important way for achieving high-density, aligned SWNTs. Figure 3a and b shows the highly oriented SWNT arrays grown on sapphire and quartz

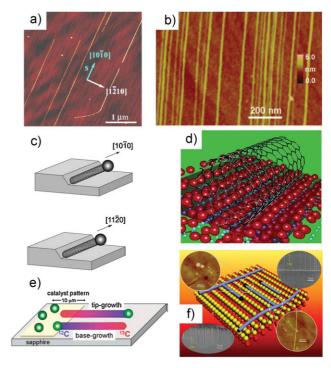


Figure 3. AFM images of perfectly aligned SWNTs on a) sapphire and b) quartz. c) Alignment of SWNTs by faceted nanosteps. a,c) Reproduced with permission from [31]. Copyright 2005, American Chemical Society. b) Reproduced with permission from [54]. Copyright 2008, American Chemical Society. d) Schematic diagram of a SWNT on an a-plane sapphire substrate along the topmost layer of oxygen atoms. Reproduced with permission from [32]. Copyright 2005, American Chemical Society. e) The resulting nanotubes expected for the base and tip growth modes when switching carbon feedstock from <sup>13</sup>CH<sub>4</sub> to <sup>12</sup>CH<sub>4</sub> during SWNT growth. Reproduced with permission from [59]. Copyright 2007, American Chemical Society. f) Using carbon nanotubes as barriers; the growth of SWNTs via lattice-oriented mode on quartz is expected to be terminated, providing a simple way to distinguish the base and tip growth modes. Reproduced with permission from [60]. Copyright 2009, Nano Research.



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substrates with anisotropic lattices or miscut atomic steps, respectively. The density of SWNTs grown in such a way reaches 22 SWNTs/ $\mu m,^{[54]}$  remarkably higher than gas-flow-directed growth. The wafer-scale synthesis of aligned SWNTs has been achieved by Zhou and co-workers. The degree of alignment and the growth efficiency strongly depend on the surface quality. In order to improve the alignment of nanotubes on substrate surface, a typical experimental treatment is to anneal sapphire at 1100 °C, and quartz at 900 °C, in air before CVD growth. A variety of metal nanoparticles has been proven by Liu and co-workers to catalyze the surface-oriented growth of SWNTs on quartz, including Fe, Co, Ni, Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, and even Mg and Al.  $^{[58]}$ 

Concerning the aligning force and high efficiency of SWNT growth on sapphire, Ismach et al. attributed these features to the formation of 1.3 nm high, faceted nanosteps on the miscut c-plane sapphire surface after annealing in air, as shown in Figure 3c. [31] These nanosteps could template the formation of a periodic array of SWNTs. On the other hand, Han et al. suggested that the crystallography of the sapphire surface was of great importance for growing aligned SWNTs and, on an a-plane sapphire surface, the carbon nanotubes would be aligned along the topmost layer of oxygen atoms (Fig. 3d).[32] On an R-plane sapphire surface, the interaction between Al atoms on the oxygen-depleted region and SWNTs was believed to be responsible for the nanotube alignment in the middle part of the wafer while the atomic steps or nanosteps were responsible for the alignment of SWNTs at the edge of the wafer.<sup>[55]</sup> The growth mechanism of aligned SWNT arrays on these crystalline surfaces is also under debate. Liu et al. supports a tip growth mechanism, [54] direct evidence of which comes from the scanning electron microscopy (SEM) observation of individual carbon nanotube ends after growth. They found that the SWNTs were terminated by nanoparticles, most possibly the catalysts, at the tube ends. There also exists evidence for a base growth mechanism. Through switching carbon feedstock from <sup>13</sup>CH<sub>4</sub> to <sup>12</sup>CH<sub>4</sub> during SWNT growth using patterned catalysts on a sapphire surface, which was expected to induce a gradient distribution of the carbon isotopes along the tube axis, Ago and co-workers visualized the growth process via Raman mapping analysis.<sup>[59]</sup> They observed a gradual change of the isotope distribution along the tube axis and found that the 12C was near the catalyst pattern, as schematically shown in Figure 3e, suggesting a base growth mode. Our results on quartz using carbon nanotubes as the growth barrier also supported the base growth mechanism. [60] As illustrated in Figure 3f, we first grew individual carbon nanotube barriers on a quartz surface via gas-flow-directed growth, which was then followed by the lattice-guided growth in the perpendicular direction. As expected, SWNTs grown by the lattice-oriented mode were terminated by hitting the nanotube barriers. AFM characterization indicated that the catalyst nanoparticles were only found at the growth 'tail' but not at the growth 'head', clearly supporting the base growth mechanism. Although it is not easy to completely exclude the existence of tip-growth tubes, we believe that the base growth must dominate over most of the nanotube growth on quartz substrates. In general, it seems that both tip and base growth mechanisms would be applicable for the aligned growth of SWNT arrays on some crystalline surfaces such as sapphire and quartz. The interaction between catalyst nanoparticles and substrate surface would play a critical role in selecting which growth mode occurs. With a stronger interaction, the catalyst nanoparticles are firmly attached to the surface, which leads to base growth. On the other hand, with a relatively weaker interaction, the catalyst nanoparticles easily slide on the surface, which results in tip growth.

Finally, compared with the gas-flow-directed growth, the length of SWNTs grown by the substrate-guided mode is generally not very long, falling into a range of hundreds of micrometers to millimeters. In addition to the higher packing density, the SWNTs obtained by surface-directed growth contain less MWNTs (multiwalled nanotubes) and bundles.

### 2.4. Combination of Different Directional Growth Modes for Complex Architectures

By a suitable design of growth process and/or a combination of different directional growth modes, various complex configurations of ultralong SWNTs can be constructed, which provides pathways for the direct growth of functional nanostructures and devices. Liu and co-workers reported the first trial in this direction.<sup>[21,22]</sup> By simply repeating the gas-flow-guided growth via fast-heating treatment, they obtained a SWNT crossbar structure as seen in Figure 4a. [21] Similar work was done by Kong and co-workers and the slight technical difference was that the crossbar structures were obtained by rotating the substrate  $90^{\circ}$ after turning off the carbon source. [23] In our recent work, [61] we succeeded in growing high-density SWNT crossbars via a one-batch process by simultaneously activating both lattice-oriented and gas-flow-directed growth modes. We found that a low temperature, (e.g., 900 °C) favors lattice-oriented growth on the quartz surface while a relatively high temperature, (e.g., 970 °C) favors the gas-flow-directed growth. Hence, there exists a trade-off of growth temperature to activate both growth modes on the quartz surface, which was found to be around 930-950 °C. With perpendicularly patterned catalyst stripes on a single-crystal, ST-cut quartz wafer (Fig. 4b), we directly grew SWNT crossbar architectures at 930 °C with ethanol as source, as seen in Figure 4c. In addition to the growth temperature, adhesion between catalyst nanoparticles and quartz substrate is another crucial factor for achieving high-quality crossbar structures. Cu catalyst, which has a relatively weaker adhesion to quartz than Fe, exhibited better performance for growing large-area and highdensity crossbars of SWNTs. With optimization of the conditions, the length of lattice-oriented SWNTs reached hundreds of micrometers with a tube spacing of a few micrometers while the gas-flow-directed SWNTs were up to millimeters long with a tube spacing of circa ten micrometers, which leads to a node density of crossed SWNTs up to 10<sup>7</sup> cm<sup>-2</sup>. [61] These SWNT crossbars may find applications in nanoelectronics for creating nonvolatile random access memory and unique logic  $devices.^{[62,63]}$ 

Another example is the growth of serpentine SWNTs. With a combinational use of gas-flow and lattice orientation forces on the quartz surface, Geblinger et al. succeeded in growing serpentine SWNTs that consisted of a series of straight, parallel, and



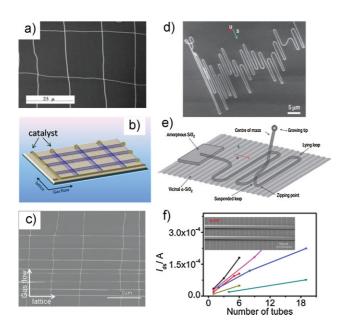


Figure 4. a) Crossbar structures of SWNTs made by a two-step, fast-heating CVD growth by Liu and co-workers. Reproduced from [21]. b) Schematic diagram of the experimental arrangement for simultaneously activating both gas-flow-directed and lattice-oriented growth modes in a one-batch process. c) SEM image of SWNT crossbar structure grown in the one-batch process shown in (b). Reproduced with permission from [61]. Copyright 2009, American Chemical Society. d) A serpentine SWNT grown on quartz by combining the gas-flow and lattice orientation forces. e) Schematic representation of the "falling spaghetti" mechanism for growing serpentine tubes. Reproduced with permission from [64]. Copyright 2008, Nature Publishing Group. f) A field-effect transistor (FET) device made from a serpentine SWNT with identical tube chirality, along with a plot of the linear dependence of device current on the number of tubes contained. Reproduced from [43].

regularly spaced segments, connected by alternating U-turns (Fig. 4d). [64] As schematically illustrated in Figure 4e, a "falling spaghetti" mechanism was proposed by the team to depict the formation of serpentine tubes. [64] The serpentines are believed to form in a two-step process, where the carbon nanotubes first grow in a floating mode, and at a later stage adsorb onto the quartz substrate in an oscillatory fashion along the surface steps, like spaghetti falling onto a tilted bamboo mat. The oscillation is induced by competition of dissipative forces of adhesion and aerodynamic drag. Such a non-equilibrium self-organization results in the formation of SWNT serpentines. The rate and direction of gas flow strongly affect the geometric structures of these serpentines.<sup>[43,64–66]</sup> By changing the angle between the direction of feeding gas flow and the surface steps (0°, 45°, 90°), Jeon et al. obtained various serpentine structures. [65] The U-turn diameters were found to be closely related to the gas flow rate and also the nanotube diameters. Obviously, to fully activate the lattice-aligning force of the quartz surface, it is better to slow down the landing process of the floating nanotubes during CVD growth. For this purpose, we designed a specific growth setup for realizing a gradual and controllable cooling of samples after switching off the carbon source. [43] With a cooling rate of 4–20  $^{\circ}$ C min $^{-1}$  from 975 to 775  $^{\circ}$ C, various structure-controlled

serpentine SWNTs were obtained with a yield of >96% using our method. It is found that the slower the cooling rate, the higher the packing density of the serpentine segments. The maximal packing density reached 2 tubes/ $\mu$ m. The magnitude of oscillated serpentines decreases with increasing gas flow rate, with a maximal magnitude being over 100  $\mu$ m.

The serpentine SWNTs provide an alternative pathway for solving the issue of chirality control. Currently it is still a great challenge to realize chirality-controlled growth of SWNTs. Suppose that we can grow an extremely long serpentine tube over a wafer surface with controllable magnitude and spacing of segments; FETs with completely identical tube chirality could then be fabricated. Demonstration of such a unique SWNT FET is given in Figure 4f,<sup>[43]</sup> in which the device current exhibited a linear increase with the number of tubes. Ultrahigh-current SWNT FET devices would be expected with optimized experimental conditions without losing the high on/off current ratio

### 2.5. Local Diameter Modulation of Ultralong SWNTs

The energy band structure of a SWNT is closely related with its diameter. For a semiconducting SWNT, the bandgap is inversely proportional to the tube diameter. Therefore, it is of great importance to realize diameter-controlled CVD growth for nanoelectronic applications. For the purpose of fabricating SWNT-based functional devices and integrated circuits, it is also essential to modulate the local band structures along the tube axis to create various intratube nanojunctions for realizing large-scale integration with one individual ultralong carbon nanotube. We developed a temperature-oscillation CVD method for this kind of axial band structure engineering of SWNTs.[24,25,67] As is well-known, temperature is a critical factor to determine the thermodynamics and kinetics of SWNT growth in the CVD process. Suppose that we drastically alter the growth temperature during the floating-mode CVD process, we would expect a certain change of the local geometric and/or energy band structures of an ultralong SWNT. Shown in Figure 5b is a successful example obtained with such a temperature-oscillation approach. [67] With a 20 °C-stepped-up temperature program from 900 to 960 °C (Fig. 5a), the diameter of a SWNT showed a stepped-down decrease from 1.68 to 1.00 nm along the tube axis, as evidenced by the up-shift of the RBM and the direct AFM measurement result. On the other hand, the local diameter of an ultralong SWNT showed an increase along the tube axis with a sudden decrease of growth temperature in a gas-flow-directed ethanol CVD process. As seen from Figure 5c, the degree of diameter change depends on the initial tube diameter, falling into a range of 0-0.4 nm. For either increase or decrease of growth temperature, the maximum diameter change was observed for a  $\sim$ 1.6 nm tube. [67]

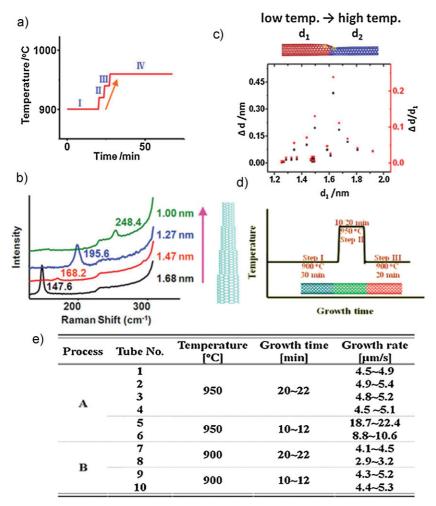
The temperature-oscillation CVD provides an effective way to directly grow intratube nanojunctions. Simply by designing the growth-temperature program, various intratube nanojunctions can be created along an ultralong SWNT. The electrical characteristics of such intramolecular nanojunctions will be discussed in Section 5. Taking account of the temperature





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**Figure 5.** a) Stepped-up temperature program used in the temperature-oscillation CVD process. b) Raman RBM peak change along an individual SWNT axis induced by temperature oscillation, suggesting a local diameter change and formation of intratube nanojunctions. c) Dependence of diameter change on the initial tube diameter measured by stepped-up temperature oscillation. Reproduced with permission from [67]. Copyright 2009, American Chemical Society. d) Temperature program designed for growth-rate measurement using temperature-oscillation CVD. e) Average growth rates of SWNTs measured at different temperatures and times. Reproduced with permission from [25]. Copyright 2007, American Chemical Society.

dependence of tube-diameter change, the temperature-oscillation method also offers an effective way to grow ultralong aligned SWNT arrays with a narrow distribution of tube diameters by designing a suitable temperature program. It is found that with a temperature-stepped-up program, the tube diameters converge to ca. 1.0 nm while they converge to ca. 2.0 nm with a temperature-stepped-down program in the available temperature range. Such kinds of SWNT arrays with narrow diameter distribution are expected to improve the performance of corresponding FET devices.

In addition, the formation of intratube nanojunctions within an ultralong SWNT offers a unique approach to measuring the absolute growth rate of carbon nanotubes.<sup>[25]</sup> As shown in Figure 5d, the stepped temperature program generates two intratube nanojunctions, which are used as markers to determine the growth length within a certain growth time. The markers can

be easily identified by micro-Raman mapping along the tube axis. The average growth rate of an individual carbon nanotube at a given temperature is then readily calculated (Fig. 5e). The results show that the growth rate falls into a range of ca. 1–20  $\mu m\ s^{-1}$  at 900–950  $^{\circ} C$  with a floating-mode ethanol CVD growth. As anticipated, the higher the growth temperature, the larger the growth rate while the growth becomes slowed down with time.

### 2.6. Chirality Control of SWNTs

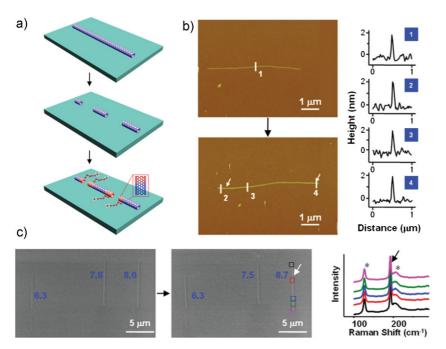
Chirality control is one of the great challenges for SWNT growth. Generally speaking, one can only obtain a mixture of SWNTs with different chiralities using conventional growth techniques. Although some progress has been achieved recently for partially controlling the electronic types (i.e., metallic and semiconducting) in the SWNT growth by B/N doping, [68] introducing methanol in the growth process,<sup>[69]</sup> and in situ UV irradiation,<sup>[70]</sup> little has been done on the ultimate control of tube chirality. Our recent work on cloning growth of SWNTs provides a pathway to approach this dream.<sup>[71]</sup> Figure 6a depicts the general strategy of cloning growth. The key of cloning growth is to use a shortened open-end SWNT as the seed or catalyst in the CVD growth process instead of conventional metallic nanoparticles. At a suitable growth temperature,  $C_x$  radicals generated from CH<sub>4</sub>/C<sub>2</sub>H<sub>4</sub> carbon source (mainly C2 and C3) are expected to directly add to the activated open end of the parent tube, leading to the elongation of the parent nanotube. The elongated segment would be expected to follow the original chirality of the "seed" tube. Therefore, we call it a cloning growth method.<sup>[71]</sup> The open-end carbon nanotube seeds were obtained from individual

ultralong SWNTs by electron beam lithography (EBL) and oxygen plasma etching, followed by thermal annealing treatment at 700 °C to get rid of -COOH and -OH groups at tube ends. Figure 6b exhibits the typical cloning growth results performed on a SiO<sub>2</sub>/Si substrate. For over 600 "seed" tubes, 56 tubes were observed to be elongated in length, with the maximum length increase being 4.6 µm. AFM and micro-resonance Raman spectroscopy characterization indicated that the duplicate nanotubes have completely the same diameters and chiralities as the original seed tubes. Similar results have been obtained on a quartz substrate via a surface-directed growth mode, as shown in Figure 6c.<sup>[71]</sup> The yield of cloning growth seems to be dependent on the growth substrate. On the quartz surface, the yield of cloning reached ca. 40% but the length increase was less than  $1 \mu m$ , while on the SiO<sub>2</sub>/Si surface, it was only ca. 9%. We found that a relatively higher temperature is necessary for the cloning



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**Figure 6.** a) General strategy of cloning growth for controlling the chirality of SWNTs. b) Cloning growth on a SiO<sub>2</sub>/Si surface, with the top left and bottom left being the AFM images for the same open-end tube before and after growth, and the right figure being the height profiles of the nanotubes marked on the AFM images. c) Cloning growth on quartz surface: two SEM images show before and after growth and the right image is the corresponding Raman RBM bands measured along the tube axis of the single tube marked with an arrow in the center image. Reproduced with permission from [71]. Copyright 2009, American Chemical Society.

growth as compared to the conventional CVD growth of SWNTs. No cloning growth was observed below 945 °C, which may support the open-end growth mechanism because the open ends of seed tubes need to be activated at higher temperature. On the other hand, the choice of carbon source is also critical. No cloning occurred without introducing  $C_2H_4$  into  $CH_4$  gas while more  $C_2H_4$  led to the formation of amorphous carbons. Further improvements are underway to obtain longer duplicate SWNTs with higher yield.

In summary, great progress has been made in the last decade on the growth of aligned, ultralong SWNTs. The direction, density, and length of these aligned SWNTs have been well-controlled with the use of suitable alignment forces. Although the maximum length is reaching a 10 cm scale, even longer SWNT arrays are definitely preferred for application purposes. As for the effective control of diameter and chirality of SWNTs, we are still in the very preliminary stages and greater efforts are desired. The window for the precise control of the growth process would be opened gradually, together with greater microscopic understanding of the catalytic CVD growth mechanism.

# 3. In situ Identification and Separation of Ultralong Metallic and Semiconducting SWNTs

Due to the lack of tube chirality control in the nanotube growth process, the as-synthesized SWNTs are a mixture of metallic (m) and semiconducting (s) tubes. In spite of their similar molecular

structures, m- and s-SWNTs are remarkably different in band structure, vibration mode, and chemical reactivity.[3,72] As already mentioned, the centimeter-scale ultralong SWNTs with the same diameter and chirality provide an opportunity to fabricate and integrate millions of electronic devices with uniform performance, which is a great attraction for nanoelectronics. Nevertheless, it is still a challenging issue to find an effective way to separate the m- and s-SWNTs. Although a number of separation strategies have been reported for SWNTs dispersed in solution, [42,73,74] for the surface-located, ultralong SWNT arrays, specific in situ separation techniques need to be developed as otherwise dispersion or dissolution of SWNTs into a liquid medium would bury the beauty of this unique system. In this section, we will focus on the identification and separation strategies compatible with ultralong surface-confined SWNTs.

### 3.1. In situ Identification of SWNTs

Electrical measurement and Raman spectroscopy are the conventional techniques for identifying SWNTs on substrate surfaces, but

they have some limitations. For example, complicated lithographic processes are involved in making metal contacts to SWNTs for electrical measurements while, for Raman spectroscopy, only those tubes that are resonant with the incident laser can be "seen". In particular, both of these approaches are time-consuming, tube-by-tube identification techniques. Very recently, electrochemical approaches are reported for the in situ identification of surface-confined ultralong m- and s-SWNTs;<sup>[75–77]</sup> this process provides a unique pathway to batch-like simultaneous identification of all nanotubes on the wafer surface.

### 3.1.1. Electrical Measurements

The different band structures of m- and s-SWNTs result in their distinct electrical transport behaviors. For m-SWNTs, the conduction and valence bands cross at the Fermi level, which makes them an ideal quasi-one-dimensional channel for electron transport, while the quasi-metallic SWNTs show curvatureinduced tiny bandgaps. On the other hand, s-SWNTs show bandgaps between the conduction and valence bands, which range from tens of millielectronvolts to several hundreds of millielectronvolts, depending on tube diameter. As already mentioned above, the bandgap of an s-SWNT is inversely proportional to the tube diameter. These differences in band structure lead to the different drain current–gate voltage  $(I_{ds}-V_g)$ dependencies when an SWNT works as conduction channel in a FET. For semiconducting tubes, there is an obvious on and off state in the  $I_{\rm ds}$ - $V_{\rm g}$  characteristics, the on/off current ratios range from 10<sup>2</sup> to 10<sup>6</sup>, depending on their bandgaps. While for metallic



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tubes, the source–drain current only shows weak gate-voltage dependence, and the quasi-metallic tubes exhibit a dip in their  $I_{\rm ds}{-}V_{\rm g}$  characteristics.  $^{[78,79]}$ 

### 3.1.2. Raman Spectroscopy

Raman spectroscopy has been widely used to obtain structural and electronic information of SWNTs. The typical Raman spectral features of an isolated SWNT involve the RBM, the G-band, the disorder-induced D-band, and its second-order harmonic (G'-band). The Raman intensity of SWNTs can be resonantly enhanced when the laser excitation energy matches the van Hove singularities (VHS) of nanotubes with a few (n,m) indices. The Kataura plot ( $E_{ii}$  vs.  $d_t$ ) summarizes the relation of VHS energy (E) for all (n,m) SWNTs as a function of tube diameter ( $d_t$ ). The tube diameter can be obtained from RBM frequency ( $\omega_{RBM}$ ) by

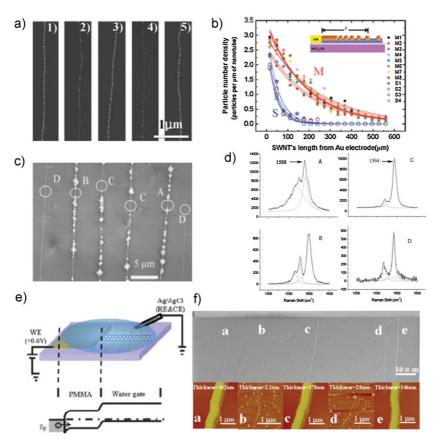


Figure 7. a) SEM images of Ag-decorated SWNTs showing obviously different particle distribution after electrodeposition at  $-0.6\,\mathrm{V}$  for 80 ms. (1), (3), and (5) are m-SWNTs. (2) and (4) are s-SWNTs. b) Particle number density of 12 Ag-decorated SWNTs after electrodeposition at  $-0.6\,\mathrm{V}$  for 40 ms. They are denoted as M1–M8 for m-SWNTs (solid marks) and S1–S4 for s-SWNTs (hollow marks). Solid curves are exponential decay fits of these data points. Reproduced with permission from [75]. Copyright 2008, American Chemical Society. c) SEM image and d) typical corresponding Raman spectra (types A, B, C, and D) from isolated individual SWNTs. Reproduced with permission from [76]. Copyright 2008, American Chemical Society. e) Illustration of the water gate effect on the band structure of a semiconducting tube in aqueous electrochemical system with a poly(methyl methacrylate) (PMMA) control strip. f) Electrodeposition of polypyrrole on an ultralong SWNTs array (with five SWNTs) transferred on Au electrodes and covered with a PMMA control strip. The thick tubes correspond to metallic SWNTs and the thin tubes to semiconducting SWNTs, as confirmed by electrical measurements. Reproduced with permission from [77]. Copyright 2009, The Royal Society of Chemistry.

the relation:  $\omega_{\text{RBM}} = (A/d_{\text{t}} + B)$ , where A and B are determined experimentally. The resonant VHS in the Kataura plot can be selected by laser excitation energy. The (n,m) index of a specific nanotube can thus be assigned as well as the metallic and semiconducting properties by using the Kataura plot. [80,81] Furthermore, the ratio of m- to s-SWNTs in a given sample can be measured through RBM by using various laser excitation energies.

The G-band can also be used for distinguishing metallic tubes from semiconducting ones through the obvious differences in line shapes. The line shape of the G-band is highly sensitive to whether the SWNT is metallic (Breit–Wigner–Fano line shape) or semiconducting (Lorentzian line shape).<sup>[5]</sup> Compared to the electrical measurement method, the advantage of Raman spectroscopy is obvious: it is a direct identification technique without the need of any lithographic processes. However, the

shortcomings of this approach are also very clear: It can only "see" a small portion of whole nanotubes at a given excitation laser energy by resonance. Moreover, the optical microscope in a conventional Raman system is also blind to the small diameter nanotubes because of the very limited spatial resolution. Therefore, time-consuming area mapping is usually necessary for finding the nanotubes on a large substrate surface.

### 3.1.3. Electrochemical Approach

Recently, an electrochemical technique has been developed for identifying the electronic types of ultralong SWNTs on solid surfaces. The centimeter-scale length and well-aligned features make it quite easy to connect the array of ultralong SWNTs with the macroelectrode via metal deposition. By applying a potential on the macroelectrode in a conventional electrochemical cell, electrodeposition of metal nanoparticles or thin conducting polymers can be performed on the surface-confined SWNTs. The different band structures of mand s-SWNTs would be expected to create a difference in their electrodeposition performance, [82,83] which then forms the basis of electrochemical identification of electronic types.

We did the first electrochemical identification of m- and s-SWNTs by depositing Ag nanoparticles onto the tube side walls as labels. [75] As shown in Figure 7a, the metallic and semiconducting tubes demonstrated remarkably different deposition results. The Ag nanoparticles were almost continuously deposited on metallic tubes while very few nanoparticles were observed on semiconducting tubes. The number of nanoparticles shows an exponential decay along an individual tube, from the end electrically connected to the macroelectrode to the opposite end. But the



decay rate is remarkably faster for s-SWNTs than for m-SWNTs (Fig. 7b). The following two factors are believed to account for the above observation: First, s-SWNTs have much smaller electron mean free paths than m-SWNTs. This leads to a rapid potential drop along the tube axis for s-SWNTs. Second, a gating effect of electrolyte works on the semiconducting tubes in an electrochemical system,<sup>[84]</sup> which further enhances the rapid potential drop. As a result, the electrochemical reaction on s-SWNTs is kinetically very sluggish compared with m-SWNTs. Therefore, we can easily distinguish the electronic types of SWNTs simply by looking at the electrodeposition performance of Ag nanoparticles. Similar methodology was adopted by Huang et al. in their recent publication:<sup>[76]</sup> they combined electrodeposition of metal nanoparticles with Raman spectroscopy to obtain the electronic-type information of SWNTs in great detail, based on the fact that mand s-SWNTs have different line shapes of Raman G-bands. For example, as illustrated in Figure 7c and d, the carbon nanotubes exhibited four different types of G-bands after electrodeposition of Ag nanoparticles, marked with A, B, C, and D, which correspond to typical metallic tubes, quasi-metallic tubes, typical semiconducting tubes, and quasi-insulating tubes, having more defects, respectively.

Instead of metal nanoparticles, we also utilized conducting polymers as the identification label.<sup>[77]</sup> In contrast to electrodeposition of metal nanoparticles, the electrochemical deposition of conducting polymers is usually carried out at positive

potentials. Under such experimental conditions, the s-SWNTs can be turned on by the water gate during electropolymerization process. This will flatten the electrochemical difference between m- and s-SWNTs. To solve this problem, we introduced a narrow poly (methyl methacrylate) (PMMA) control strip at the SWNTs-macroelectrode contact area by spin-coating to screen off the water gate effect. The s-SWNTs are therefore turned off at the PMMA-covered area and become more resistive to the electrochemical reaction while metallic tubes are not affected (Fig. 7e). A drastic change in electropolymerization behavior of m- and s-SWNTs was observed with the PMMA control strip. Compared with s-SWNTs, m-SWNTs were coated with a much thicker polypyrrole film under the same experimental conditions. Therefore, the conducting polypyrrole can also work well as the label for discriminating m- and s-SWNTs, as seen in Figure 7f, suggesting that there is quite a range of freedom for choosing the electrochemical identification labels.

It should be pointed out that, for ultralong SWNTs arrays, one only needs short segments (ca. tens of micrometers long) of the tubes for electrochemical identification purposes; this keeps the remainder of the tube lengths intact. Hence, the electrochemical approach is a semi-nondestructive method. Considering the emphatic difference of m- and s-SWNTs after electrodeposition,

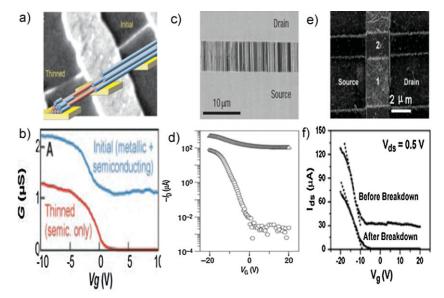
the electrochemical approach may also provide a pathway for further separation.

### 3.2. In situ Separation of m- and s-SWNTs on Surfaces

For fabricating high-performance field-effect transistors, s-SWNTs are preferred, while for interconnection purposes, one needs m-SWNTs. For surface-confined SWNTs, the strategy for most of the separation techniques is to destroy or remove m-SWNTs but to keep the s-SWNTs intact for device construction. Obviously, techniques developed for solution-phase separation, such as centrifugation,<sup>[73]</sup> dielectrophoresis,<sup>[85]</sup> and chromatography<sup>[42]</sup> are not suitable for this specific surface-confined system. The compatible techniques include electrical breakdown,<sup>[86]</sup> plasma etching,<sup>[40]</sup> light irradiation,<sup>[87]</sup> and selective covalent functionalization.<sup>[88]</sup>

#### 3.2.1. Electrical Breakdown

The electrical-breakdown method was first reported by Avouris and co-workers. [86] To selectively remove metallic tubes, a positive gate voltage was applied to turn off the semiconducting tubes and then a large bias voltage was applied to destroy metallic tubes by self-heating. This electrical-breakdown process is illustrated in Figure 8a, and the  $G(V_g)$  curves for such SWNT ropes before and



**Figure 8.** a) The electrical breakdown of SWNT ropes. b) Stressing a mixture of s- and m-SWNTs while simultaneously gating the bundle to deplete the semiconductor carriers resulted in the selective breakdown of the m-SWNTs. The  $G(V_g)$  curve rigidly shifted downward as the m-SWNTs were destroyed. The remaining current modulation is wholly due to the remaining s-SWNTs. Reproduced with permission from [86]. Copyright 2001, AAAS. c) SEM image of a FET based on an array of high-density, perfectly aligned SWNTs. d) Transfer curves from a transistor that uses aligned arrays of SWNTs. The data correspond to measurements on the device before (open triangles) and after (open circles) an electrical breakdown process. Reproduced with permission from [57]. Copyright 2007, Nature Publishing Group. e) AFM image of a thin-film transistor based on a carbon-nanotube strip array with a channel length of 2  $\mu$ m. Nanotubes in region 1 remain intact while nanotubes in region 2 are removed by etching. f) Transfer characteristics of a device before and after the electrical breakdown. Reproduced with permission from [89]. Copyright 2004, American Chemical Society.



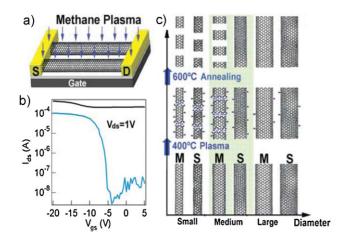
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after controlled breakdown are shown in Figure 8b. The sudden downward shift in the  $G(V_g)$  curve suggests electrical breakdown of the m-SWNTs, and the remaining current modulation is wholly arising from the remaining s-SWNTs. This simple, yet highly efficient method can improve the on/off current ratio by several orders. It has been therefore widely used not only on high-density SWNT arrays but also on random SWNT networks for high-SWNT-based thin-film transistor applications (Fig. 8c-f). [57,89,90] It should be pointed out that the breakdown operation does not mean a complete removal of m-SWNTs. Instead, it cuts the long tube by regional overheating. Moreover, accidental killing of s-SWNTs would also be possible if the breakdown voltage is not properly set. As for a chip with a large number of transistors, this electrical-breakdown method seems helpless and a batch-like removal of m-SWNTs is preferred.

### 3.2.2. Plasma Etching

Compared with the electrical-breakdown method, the plasma-etching approach is more efficient in selectively removing metallic SWNTs and obtaining pure semiconducting SWNTs on substrates. Both methane plasma<sup>[40]</sup> and hydrogen plasma<sup>[91]</sup> have been utilized as the etching reagents. Dai and co-workers first demonstrated that the methane-plasma treatment can result in selective removal of m-SWNTs and diameter distribution narrowing of SWNTs (Fig. 9a and b).<sup>[40]</sup> By exposing the few-tube devices to methane plasma at 400 °C and then annealing the devices at 600 °C in vacuum, they observed the selective etching of SWNTs. They found that the etching effect of methane plasma was sensitive to the tube diameters. Briefly, only the medium-diameter (1.4 nm < d < 2 nm) m-SWNTs were selectively etched or removed over semiconducting ones, while the smaller diameter tubes experienced nondiscriminate etching for both



**Figure 9.** a) Schematic of the methane-plasma treatment for selective etching of metallic carbon nanotubes from the gas phase. b) Current versus gate voltage ( $I_{\rm ds}-V_{\rm gs}$ ) characteristics ( $V_{\rm ds}=1\,\rm V$ ) of the device before (black curve) and after (blue curve) treatment. c) Illustrations of the fate of metallic and semiconducting SWNTs in different diameter regimes. In all cases, the annealing step reverses covalent functionalization (represented by species drawn on the tubes after the plasma step) on the retained SWNTs. Reproduced with permission from [40]. Copyright 2006, AAAS.

m- and s-SWNTs; the plasma etching was ineffective on larger diameter tubes regardless of the tubes being metallic or semiconducting (Fig. 9c). They believed that the higher radius of curvature and higher strain in the C-C bonding configuration of small-diameter SWNTs made them preferentially etch over large-diameter tubes. The reason for selective etching in the medium-diameter region can be attributed to the lower formation energies of s-SWNTs than m-SWNTs at the same diameter because of the bandgap opening of semiconducting tubes and the higher chemical reactivity of metallic tubes because of more abundant delocalized electronic states. By increasing the number of SWNTs in the channels and controlling the tube diameters in a range of 1–1.8 nm, they succeeded in fabricating FETs with 100% yield of s-SWNTs. This "dry" chemical etching technique is scalable and compatible with traditional semiconductor processing technology, which would greatly contribute to SWNT-based nanoelectronics and macroelectronics. Dai and co-workers also studied the effect of hydrogen plasma and observed a diameter-dependent etching without metallic and semiconducting selectivity because of its high reactivity.<sup>[92]</sup> Nevertheless, a contradictory result was reported by Hassanien et al. [91] They found that the hydrogen plasma selectively diminished the m-SWNTs while leaving the s-SWNTs intact. [91] Their scanning transmission microscopy (STM) and Raman spectroscopy results demonstrated that the m-SWNTs were dramatically altered and damaged by hydrogen-plasma treatment. The reason for this inconsistency is not clear and further studies are required.

#### 3.2.3. Irradiation

Irradiation with suitable light is a clean and simple approach to sorting semiconducting SWNTs by preferential elimination of metallic tubes. So far, the reported irradiation techniques involve using different lights, such as laser (514.5 nm for Ar $^+$  and 632.8 nm for He–Ne),  $^{[93]}$  long-arc xenon lamp (0.18–11  $\mu$ m),  $^{[87]}$  and microwave (2.45 GHz).  $^{[94]}$ 

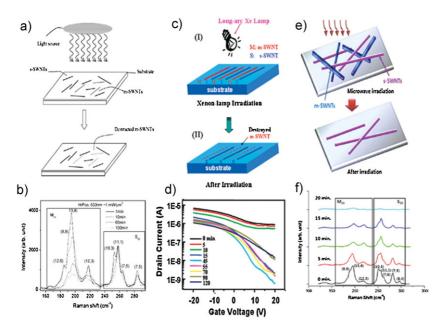
Huang et al. investigated the irradiation effect of 514.5 nm (Ar<sup>+</sup>) and 632.8 nm (He-Ne) lasers on mixed s- and m-SWNTs. [93] As shown in Figure 10a and b, with 100 min of 632.8 nm laser irradiation in air (power density 1 mW μm<sup>-2</sup>), the Raman peak at around 195 cm<sup>-1</sup>, attributable to metallic tubes (13,4), decreased by about 80% while the peak at 257 cm<sup>-1</sup>, originating from semiconducting tubes (11,1), remained essentially unchanged. Their work indicates that m-SWNTs can be preferentially destroyed with a suitable laser and the SWNTs with higher chiral angles are more sensitive to laser irradiation. As a similar strategy, we employed a long-arc xenon lamp to selectively destroy metallic carbon nanotubes in high-density and well-aligned SWNT arrays (Fig. 10c). [87] It was found that, for SWNTs with a diameter of 1.15-1.55 nm, 60 min irradiation brought about a drastic increase of s-SWNTs from ca. 50 to 95%. Hence, simply by increasing the irradiation time, the on/off current ratio of the SWNT-array FET device increased from less than 10 to over 2000 (Fig. 10d).

Microwave irradiation was also found to preferentially eliminate m-SWNTs in the pristine SWNTs mixture. [94] As demonstrated in Figure 10e and f, after irradiation for 10–15 min, the Raman intensity of the radial breathing modes of m-SWNTs decreased by about 77% while the semiconducting tubes



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**Figure 10.** a) Schematic drawing of carbon nanotubes exposed to laser irradiation. b) Change of Raman spectra around the radial breathing mode (RBM) region for HiPco SWNTs upon 632.8 nm laser irradiation. The laser power density is about 1 mW  $\mu$ m $^{-2}$ . Reproduced with permission from [93]. Copyright 2006, American Chemical Society. c) Schematic illustration of the idea of sorting s-SWNT arrays using long-arc Xe lamp irradiation. d)  $I_{ds}$ – $V_g$  curves after different Xe lamp irradiation times (0, 5, 10, 15, 45, 75, 90, and 120 min) for a FET fabricated from SWNT arrays. Reproduced with permission from [87]. Copyright 2008, American Chemical Society. e) Schematic diagram of the process of selective destruction of metallic single-walled carbon nanotubes using microwave irradiation. f) Raman spectra around the RBM region with excitation energies of 633 nm for a pristine sample, and a residual sample after 5–20 min of microwave treatment. Reproduced with permission from [94]. Copyright 2009, IOP Publishing Ltd.

decreased only by 10%. Similar to the observation of Huang et al., [93] the metallic SWNTs with higher chiral angles were preferentially decomposed by microwave irradiation. This selective destruction of m-SWNTs may originate from the distinct dielectric constants of m- and s-SWNTs. Microwaves can selectively couple with materials that possess a high dielectric constant. Because the m-SWNTs have much higher dielectric constants than s-SWNTs, they would absorb more energy during irradiation. As a result, the metallic tubes are preferentially destroyed.

Compared with most of the complicated physical and chemical separation techniques, the irradiation approach is very simple and convenient without contamination of pristine nanotubes. However, the mechanism for chiral selectivity is not fully understood yet, and would depend on the wavelength range of the irradiation. It would also be complicated by laboratory ambient conditions such as humidity and partial pressure of  $O_2$ . Unexpected damage of s-SWNTs would happen under light irradiation, which degrades the excellent performance of s-SWNT FET devices.

### 3.2.4. Selective Covalent Functionalization

Covalent functionalization of SWNTs with chemical groups offers more opportunities to separate metallic tubes from semiconducting ones. Metallic and semiconducting SWNTs are expected to

show different chemical reactivities because of their distinct electronic structures. A representative example was demonstrated by Strano et al. using diazonium reaction.<sup>[74]</sup> They found that water-soluble diazonium salts can extract electrons from SWNTs to form covalent aryl bonds (Fig. 11a and c). The reaction process involves the formation of a charge-transfer complex between diazonium cations and the carbon nanotube surface, where electron donation from nanotube stabilizes the transition state and accelerates the forward reaction rate. The extent of electron transfer is dependent on the density of states near the Fermi level. As a result, the m-SWNTs showed higher reactivity than s-SWNTs (Fig. 11b). Once the bond symmetry of the nanotube is disrupted by the formation of the defective transition complex, the chemical reactivity of adjacent carbon atoms on the nanotube surface will be increased. Therefore, the initial chiral selectivity would be amplified as the entire nanotube is chemically functionalized. Subsequent research by many groups indicate osmium tetroxide, azomethine ylides,<sup>[96]</sup> hydrogen peroxide,<sup>[97]</sup> nitric and sulfuric acids, [98] fluorine gas, [99] reductive alkylation,<sup>[100]</sup> halogen oxoanions,<sup>[101]</sup> and fluorinated polyolefins<sup>[102]</sup> also selectively react with metallic SWNTs.

By selective covalent modification, the m-SWNTs could be electronically disabled. This provides an easy way to improve the

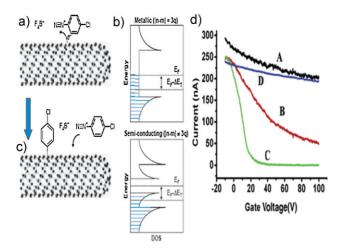
performance of SWNT FETs. Figure 11d demonstrates such an example by An et al., who used the diazonium reaction.<sup>[88]</sup> The SWNT FET device was simply immersed in aqueous 4-bromobenzenediazonium tetrafluoroborate solution with enough stirring. As the reaction proceeded, the p-type transfer characteristics became greatly improved with a remarkable increase of on/off current ratio. This suggests that the metallic nanotubes have been electronically destroyed by selective chemical functionalization. More interestingly, the diazonium functionalization is chemically reversible. After annealing, the transfer characteristics almost recovered. Similar selective suppression of conductance of surface-confined m-SWNTs was realized by chemical modification with 4-bromobenzene diazonium tetrafluoroborate (4-BBDT), nitronium tetrafluoroborate (NO<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>), 2,4,6-triphenylpyrylium tetrafluoroborate (2,4,6-TPPT), and 1,3-benzodithiolylium tetrafluoroborate (1,3-BDYT).<sup>[88]</sup>

An electrochemical approach has also been utilized for selective covalent modification of metallic SWNTs. In a FET configuration, the s-SWNTs can be switched to the off state by gating. Balasubramanian et al. found that the stability of this off state can be maintained for approximately 10 to 15 min. [103] After SWNTs were switched to the off state, electrochemical modification was achieved by applying a  $-280\,\mathrm{mV}$  potential to SWNTs vs. platinum for 30 s in a 10 mm 4-nitrobenzene diazonium salt solution in N,N-dimethylformamide (DMF), with 0.1 m lithium



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**Figure 11.** a) Diazonium reagents extract electrons, thereby evolving  $N_2$  gas and leaving a stable C–C covalent bond with the nanotube surface. b) The extent of electron transfer is dependent on the density of states in that electron density near the Fermi energy level ( $E_F$ ), which leads to higher initial activity for metallic and semimetallic nanotubes. c) The arenefunctionalized nanotube may now exist as the delocalized radical cation, which could further receive electrons from neighboring nanotubes or react with fluoride or diazonium salts. Reproduced with permission from [74]. Copyright 2003, AAAS. d) Gate dependence curves of the device; A) before the diazonium reaction, B) after the first reaction with the diazonium reagent ( $5.3 \times 10^{-7} \, \mu \text{M}$ ), C) after a second reaction ( $5.3 \times 10^{-7} \, \mu \text{M}$ ), and D) after annealing. The bias was 100 mV. Reproduced with permission from [88]. Copyright 2004, American Chemical Society.

perchlorate as background electrolyte. The following I-V measurements indicated that m-SWNTs showed a strong increase of resistance by four orders of magnitude while the performance of s-SWNTs remained nearly the same. Using this strategy, Balasubramanian et al. have succeeded in fabricating high-performance s-SWNT FETs from a mixture of m- and s-SWNTs. $^{[103]}$ 

### 3.2.5. Metal-Semiconductor Transition

Most of the separation techniques reported up to now lead to the sacrifice of metallic SWNTs. Undoubtedly, the best choice is to convert metallic nanotubes into semiconducting ones. In principle, it would be possible to open the bandgaps of m-SWNTs through chemical bond engineering of sp<sup>2</sup> carbon atoms in the one-dimensional  $\pi$ - $\pi$  conjugation system. Both theoretical calculations and experimental studies have demonstrated that deformation can induce semiconductor-metal or metal-semiconductor transitions in SWNTs.[104-106] It was also found that some covalent chemistry on the sidewall of m-SWNTs could open a gap at the Fermi level and change metallic tubes into semiconducting ones by introducing defect sites.<sup>[107,108]</sup> Moreover, low-energy electron irradiation was found to induce the metal-semiconductor transition in SWNTs, which may be due to the modulation of SWNTs' band structure by local inhomogeneous electric fields that arise from charging during electron irradiation.<sup>[109]</sup> Recently, the transition of SWNTs from metallic to semiconducting was realized by hydrogen-plasma treatment.<sup>[41]</sup> When the SWNT FET was treated with hydrogen plasma, hydrogen atoms could be adsorbed on the nanotube sidewalls, which led to the bandgap opening of metallic tubes. This conversion was found to be reversible by a standard annealing process. An on/off ratio change from 3–10 to 100–1000 was achieved by hydrogen treatment. It should be pointed out that, although the hydrogen-plasma treatment can effectively convert metallic SWNTs into semiconducting ones, it also results in degradation of the FET performance by on/off ratio decrease because of the damage to semiconducting tubes. They found that for s-SWNTs, the hydrogen treatment could lower the on/off ratio from >100 to >10.  $[^{41}]$ 

Generally speaking, for most of the separation techniques mentioned above, the diameters of SWNTs play an important role, or in other words, the separation efficiency is strongly dependent on tube diameter. In most cases, effective separation of m- and s-SWNTs is achieved with diameters of a middle range. No matter what techniques are employed, the key is to induce a chemical reaction on the sidewalls of SWNTs. The reactivity of SWNTs is determined by two crucial factors: the strain in C-C bonding and the density of states near the Fermi level. The higher curvature of small-diameter SWNTs results in the higher reactivity of both metallic and semiconducting tubes. Hence selective chemical reactions can not be expected for smalldiameter tubes. On the other hand, the lower curvature of large-diameter SWNTs dulls the reactivity of both m- and s-SWNTs and therefore leaves them nearly inert to chemical treatments. It is only in the medium-diameter regime that the density of states near the Fermi level can dominate the reactivity of SWNTs and lead to a high reaction selectivity between m- and s-SWNTs. Unfortunately, the diameter control and/or separation of surface-confined ultralong SWNTs is a great challenge at present. And things become worse when one considers the co-existence of MWNTs and bundles produced in the growth process of ultralong SWNTs. Therefore, more efforts are needed for developing effective techniques for the separation of metallic and semiconducting nanotubes together with the chirality- and diameter-controlled synthesis of ultralong SWNTs.

# 4. Transfer Printing and Manipulation of Ultralong SWNTs

As a result of the high-temperature process during CVD, only a few substrates can be directly used as the supporting substrates for growing ultralong SWNT arrays; this factor limits the application of CVD-grown nanotubes in electronics. The most widely used substrates include silicon, silicon with thermally grown oxide layers, quartz, sapphire, and silicon nitride. Motivated by the demands of obtaining ultralong carbon nanotubes on desired substrates, including physically or chemically patterned substrates, a number of techniques have been developed to transfer the CVD-grown SWNT arrays from source substrates to various designed substrates. [110-114] The idea of most transfer approaches is based on the utilization of a transfer-printing mediator to keep the original SWNT-array structures or architectures and print them onto the target substrate surface. Generally, the transfer-printing process involves three sequential steps: First, the SWNTs grown on the source substrate are transferred onto the transfer-printing mediator. Second, the transfer-printing mediator carrying the



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SWNTs is made to closely attach to the target substrate surface in a well-controlled manner. Finally, the mediator is removed from the target substrate to release the SWNTs onto the target substrate surface. Besides the transfer of SWNTs, these approaches are also used to create complex structures of SWNTs and to integrate SWNTs into hybrid structures with other nanoscale building blocks. [112,113] The morphology of the SWNT arrays could also be manipulated via the transfer-printing mediator. [115,116] Further development made it possible to place individual SWNTs with specific chiralities on exact surface locations for fabricating purpose-directed electronic devices and circuits in a well-controlled fashion. [117–119]

### 4.1. Transfer Printing of SWNTs

The key of the transfer-printing technique is the choice of a suitable transfer-printing mediator, which determines the yield, fidelity, and controllability. Polymers, such as poly(dimethylsiloxane) (PDMS)<sup>[110–112]</sup> and PMMA,<sup>[113]</sup> and metals, such as gold and chromium,<sup>[114,120]</sup> have been employed for this purpose. These mediators fall into two categories: insoluble (PDMS) and soluble (PMMA and metals). The procedures, mechanism, advantages, and limitations of these approaches are briefly described in this section.

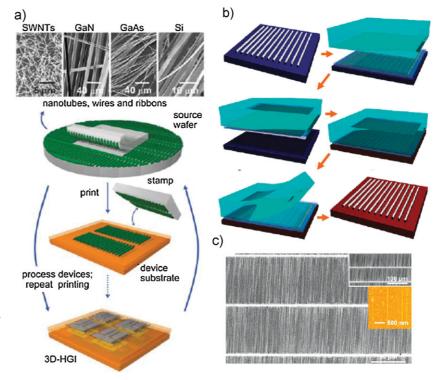
### 4.1.1. Transfer Printing with PDMS

The PDMS stamp is widely used for printing micro- and nanoscaled patterns of organic molecules onto substrates by the micro-contact printing ( $\mu$ -CP) technique developed by Whitesides and co-workers. [121,122] Rogers and colleagues extended the  $\mu$ -CP technique to transfer various nano- and micrometersized materials/structures with the PDMS stamp. [111,112,123,124] Figure 12a illustrates this PDMS-mediated transfer-printing technique.[112] The PDMS stamp is first contacted to the source substrate to adhere the target nanomaterials by van der Waals interactions. After carefully detaching from the source substrate, the stamp with nanomaterials is then pressed onto the desired substrate surface. Finally, the nanomaterials are printed onto the target substrate simply by removing the stamp. This transfer-printing process is based on kinetically controlled switching between adhesion and release of nanomaterials to and from the PDMS stamp. By controlling the rate of separating stamps from the source and target substrates, a high transfer yield can be achieved.[111] This approach has been used to transfer SWNTs, nanowires, nano- and microscaled ribbons, graphene, and other structures to various substrates.<sup>[111,112]</sup> However, the yield of transferring nanoscaled building blocks such as SWNTs is lower than that for microscaled objects. The pressure introduced during

transfer printing may deform the target objects. Moreover, the PDMS-based approach has limitations in creating complex nanoarchitectures via multiple transfer-printing operations. In a sequential, multiple transfer-printing process, the PDMS stamp will pick up the pre-transferred objects when separating from the target substrates without the use of a protecting layer.

### 4.1.2. Transfer Printing with an Intermediate Metallic Film

Rogers and co-workers made some improvements to the PDMS-mediated transfer-printing technique by adding a metal film to directly contact the SWNTs. They deposited 2 nm Cr and 20 nm Au on the SWNTs, grown on a SiO<sub>2</sub>/Si substrate, and then patterned the metal film with lithographic and etching techniques. After that, the SiO2 layer was removed by hydrofluoric acid. Then the PDMS stamp was used to transfer the metal film with SWNTs onto plastic substrates. Finally, the metal film was dissolved by commercial etchant (Au-TFA for etching Au and CR-7 for Cr). [120] In their subsequent work, [114] they further modified this method by using Au, polyimide (PI), or polyvinyl alcohol (PVA) film as the intermediate transfer-printing mediator instead of Cr/Au for transferring aligned SWNTs. Figure 12b and c shows the schematic of this approach and the resultant aligned SWNTs transferred from quartz to SiO<sub>2</sub>/Si, respectively. The coverage and geometry of tubes are well-maintained. The modified PDMS-based approach is capable of multiple transferprinting operations and can yield well-defined multilayer



**Figure 12.** a) Schematic for transferring nanomaterials from source substrates to device substrates and making three-dimensional devices with PDMS stamps. Reproduced with permission from [112]. Copyright 2006, AAAS. b) Schematic for transferring aligned SWNTs arrays with Au/PI (polyimide) film as mediator. c) Aligned SWNTs were transferred to  $SiO_2/Si$  substrates from quartz via the method shown in (b). Reproduced with permission from [114]. Copyright 2007, American Chemical Society.



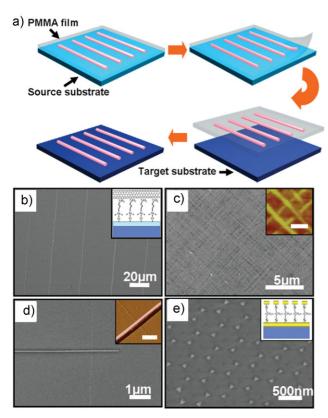
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superstructures of SWNTs. Two-layer crossbars and three-layer triangle lattices of SWNTs have been successfully fabricated using this approach. The utilization of a metallic mediator improved the transfer yield and enabled multiple transfers. The weak point of this method is that the removal of metal with oxidative etchant would degrade the intrinsic properties of SWNTs. In addition, the involvement of lithographic procedures such as metal deposition, microlithography, and chemical etching also makes the process complicated and time-consuming.

### 4.1.3. Transfer Printing with PMMA

To improve the yield, fidelity, and quality of transfer printing, we developed a universal nanotransfer-printing technique that uses a flexible PMMA thin film as the transfer-printing mediator. The transfer process involves four steps, as shown in Figure 13a, including spin-coating a PMMA thin film onto the source substrate, which is preloaded with nanoscale building blocks such as SWNTs, peeling the PMMA mediator from the source substrate by alkaline treatment, attaching the mediator to a target substrate in a controlled fashion, and finally releasing the nanomaterials to the target substrate by removing the PMMA thin film with acetone vapor or thermal decomposition. The



**Figure 13.** a) Illustration of the procedures involved in the PMMA-mediated nanotransfer printing technique. b) Ultralong SWNT array transferred onto the APTS monolayer-modified Si surface. c) High-density crossbar array of SWNTs. Inset: AFM image of the cross junction. Scale bar: 50 nm. d) Heterogeneous cross junction of ZnO nanowire and a semiconducting SWNT. Inset: AFM amplitude image of the junction, scale bar 200 nm. e) Triangular gold nanosheet/SAM/gold film sandwich structures. Reproduced with permission from [113]. Copyright 2008, American Chemical Society.

typical thickness of PMMA film is 200-300 nm and is obtained by spin-coating 4 wt% PMMA solution at 3000 rpm. With this PMMA-mediated approach, we have successfully transferred many nano- and microscale building blocks onto various commonly used substrates, achieving 100% yield. [113,118] For example, aligned ultralong SWNTs can be transferred with excellent fidelity from Si, SiO2/Si, Si3N4/Si, quartz, and sapphire surfaces onto flat, patterned, curved, and flexible substrates. The typical architectures made by PMMA-based transfer printing are given in Figure 13b-e, including an SWNT array on an organic self-assembled monolayer (SAM) (Fig. 13b), which allowed the direct observation and modulation of SWNT photoluminescence on the substrate surface, [125] high-density crossbar array of SWNTs (Fig. 13c), hybrid n-ZnO nanowire/p-SWNT cross junction (Fig. 13d), and gold nanosheet/SAM/gold sandwich structure (Fig. 13e).

Compared with the rigid PDMS stamp and metallic mediators, the flexible PMMA film has some prominent advantages. First, the SWNTs and other objects are embedded into the flexible PMMA film in the transfer process. This physical encapsulation in addition to van der Waals interactions ensures a 100% loading efficiency and faithful transfer. Second, PMMA is soluble in acetone and thermally decomposable at relatively low temperatures. Hence its removal with such kinds of treatment would not disturb the pre-transferred architectures. As a result, complex architectures can be created via multiple transfer-printing operations of homo- or heterogeneous nanoscale building blocks. Such a mild removal treatment maintains the pristine properties of nanomaterials and substrates. Moreover, this PMMA-mediated approach also holds similar advantages to the PDMS-based approach, such as simplicity, controllability, and universality to target objects and substrates. This nanoscale brick-laying technique paves the way to generate purpose-directed nanoarchitectures with homo- or heterogeneous building blocks; access to such structures facilitate exploration of their fundamental properties and the building of novel devices.

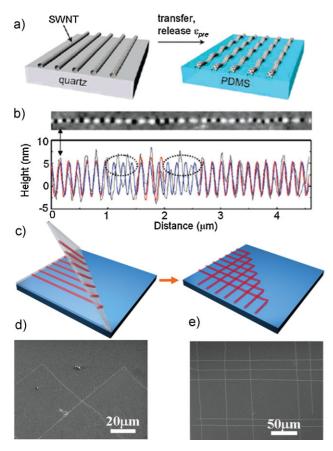
## 4.2. Manipulation of SWNTs via the Transfer-Printing Approach

AFM is frequently utilized to manipulate SWNTs on surfaces. By using AFM tips, one can translate, roll, bend, stretch, and twist surface-confined carbon nanotubes; these operations induce various local deformations on the nanotubes. The mechanical flexibility of polymeric transfer-printing mediators described above offers an alternative way to manipulate the SWNTs on surfaces and allows for fabrication of unique structures using SWNTs.

### 4.2.1. Buckling Structures of SWNTs with PDMS

Rogers and co-workers transferred SWNT arrays onto a mechanically pre-stretched PDMS stamp. After that, they released the PDMS and created wavy SWNTs structures, in which the tube height varies periodically along the tube axis (Fig. 14a and b). The wave periods were 100–300 nm, with amplitudes of several nanometers. Their results demonstrated the possibility of mechanically manipulating SWNTs





**Figure 14.** a) Schematic for fabricating molecular-scale SWNTs buckling with pre-strained ( $\epsilon_{\rm pre}$ ) PDMS stamps. b) AFM image and height profile of buckled SWNTs. Reproduced with permission from [115]. Copyright 2008, American Chemical Society. c) Schematic for manipulating ultralong SWNTs with PMMA film. d,e) SEM images of an array of bent SWNTs and a crossbar array of SWNTs, respectively, obtained with the method shown in (c). Reproduced with permission from [116]. Copyright 2008, American Chemical Society.

structures at the molecular scale. Such types of strained SWNTs can be used as stretchable conductors and strain-coupled electronic devices.

### 4.2.2. Manipulation of SWNTs with PMMA

The excellent flexibility of the PMMA thin film provides more freedom to manipulate the ultralong SWNTs loaded on it. As schematically shown in Figure 14c, a well-controlled bending of SWNTs can be performed simply by macroscopically folding the supporting PMMA film; this has been demonstrated in our recent work. [116] The bending angles of SWNTs were well-defined by controlling the folding angles of PMMA film. And the PMMA mediator could be removed using acetone vapor or thermal decomposition treatments. Bent SWNTs with a wide range of bending angles, from smaller than 10° to nearly 180° have been obtained with this approach. Accompanied with the creation of arrays of bent SWNTs (Fig. 14d), SWNTs crossbar structures were formed in the unbent region (Fig. 14e). The pristine properties of bent SWNTs were not degraded by this kind of manipulation as a

result of the protection of the PMMA film. Complicated 2D architectures such as SWNT arrays with step-like and zigzag structures have been created by multiple folding of the PMMA mediator with the aid of micromanipulator. These complex architectures of SWNTs may add new degrees of freedom for building unique electronic devices and nano-electromechanical systems (NEMS).

### 4.3. Controlled Placement and Integration of SWNTs by Transfer Printing

Achieving the breakthrough of integrating individual SWNTs into circuits is vital to their practical application in nanoelectronics. The technological difficulties of fabricating practical scalable SWNT-based circuits arise not only from controlling the chirality and geometry of SWNTs but also from positioning specific SWNTs on a wafer surface in a designed way. At present, only a few approaches have been proposed to place individual SWNTs with specific chirality at exact locations by directly transferring (mechanically or with the aid of a PMMA film) as-grown suspended SWNTs from source substrates to target substrates. [117–119] These technological explorations aim at selectively handling individual SWNTs in a well-controlled fashion for fabricating purpose-directed electrical circuits.

### 4.3.1. Controlled Placement of SWNTs by Specially Designed Substrates

Huang et al. reported a direct mechanical transfer technique for placing specific SWNTs at exact locations. [117] As shown in Figure 15a and b, their approach started from growing long SWNTs across a narrow slit, which had been etched through a Si wafer. The suspended sections of the tubes were characterized optically to determine their electronic structures. After that, a specific tube with desired properties was selected and all other tubes were burnt away by laser. After coating gold pads at the

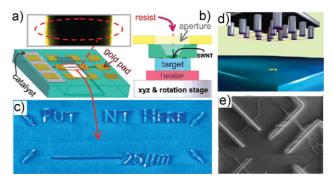


Figure 15. a,b) Schematics for placment of individual ultralong SWNTs by contacting the suspended tubes to the target substrates with an aligner. c) SEM image of an ultralong SWNT placed on the target substrate with markers. Reproduced with permission from [117]. Copyright 2005, American Chemical Society. d) Schematics for placing networks of SWNTs, grown on Si pillars, onto substrates with predefined circuits to obtain devices. e) SEM image of a patterned CNT device architecture system created using the method shown in (d). Reproduced with permission from [119]. Copyright 2007, American Chemical Society.

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suspended tube ends, the whole chip was inverted, put into contact with the target chip at the desired location with the help of a mask aligner. Then the selected specific SWNT was transferred onto the target chip surface by a drop of resist. Finally, the resist was gently removed by solvent, leaving the tubes on the target substrate. Figure 15c exhibits the typical result thus-obtained with a resolution of  $\sim\!\!1\,\mu m$ . With this approach, they fabricated FETs and cross junctions with specific SWNTs.

A similar strategy was employed by Abrams et al. for creating predefined networks of individual SWNTs (Fig. 15d). [119] In their work, the SWNTs were grown between microfabricated silicon pillars to form suspended networks of SWNTs, followed by Raman spectroscopic mapping to reveal the electronic properties of the SWNTs. This nanotube network was then transfer-printed onto a chip with prefabricated electrode patterns to generate transistors and complicated electronic devices while maintaining the pristine structures of the network components (Fig. 15e). This approach provides a comprehensive and scalable way to create large-scale electronic devices though the low growth and transfer yields would limit its application.

The above two approaches allow for precise placement of individual SWNTs or networks with desired properties. However, utilization of specially structured substrates introduces severe restriction on the geometry and length of SWNTs to which it can be applied. The essential mechanical contact of two solid surfaces in these approaches would also disturb and even damage the transferred SWNTs.

### 4.3.2. Controlled Positioning and Integration of SWNTs with a PMMA Mediator

Using flexible and transparent PMMA thin film as a macroscopically handlable mediator, we achieved precise positioning of ultralong SWNTs with specific chiralities on arbitrary surfaces. This has enabled us to fabricate various SWNT-based electronic devices by selectively positioning metallic, p- and n-type semiconducting tubes onto predefined electrode patterns.[118] As schematically illustrated in Figure 16a, this approach starts by loading SWNTs with desired properties onto the PMMA mediator. Then the mediator is driven to contact the target substrate at the desired location with an aligner system. Finally, the PMMA film is removed to release the SWNTs onto the target surface. Arbitrary architectures and devices with specific SWNTs can be constructed by repeating the above operations. The transparency and marker-replicating capability of the peeled-off PMMA-SWNTs film offer the possibility of positioning SWNTs to exact locations on target surfaces with the aid of a marker aligner, which is composed of an optical microscope and an XYZ-movable stage. In the case shown in Figure 16, the selection of nanotubes with specific chirality from an ultralong SWNT array was done by Raman spectroscopy mapping. The accuracy of tube

positioning is determined by the optical aligner system, which is approximately  $1\,\mu m$  in our work (Fig. 16b and c). This PMMA-based approach is compatible with multiple operations and also tolerant with p–n conversion by chemical doping; all of which allows for construction of complicated purpose-directed logic circuits. The typical electronic devices and circuits made by specific SWNTs are shown in Figure 16d and e, including a  $2\times 2$  all-nanotube crossbar circuit and a CMOS inverter. Nevertheless, the transfer-printing-based approaches demonstrate low efficiency and are time-consuming, both of which need further improvement for large-scale production.

# 5. Electronic Devices Based on Ultralong Aligned SWNTs

One of the most attractive applications of SWNTs is in high-performance nanoelectronic devices because of their long carrier mean free length<sup>[130–132]</sup> and high carrier mobility. <sup>[133–135]</sup> Ultralong, aligned SWNT arrays are believed to be the best material platform for this purpose. Suppose that we have a well-aligned array of SWNTs on a wafer surface, we may easily fabricate millions of FETs along each individual tube axis and achieve large-scale integration by suitable tube—tube interconnections. Using the transfer-printing techniques described above, complex 2D and even 3D functional architectures would also be possible. Here we first introduce the basic electrical transport properties of ultralong SWNTs, followed by a discussion of the experimental approaches to modulating the local band structures

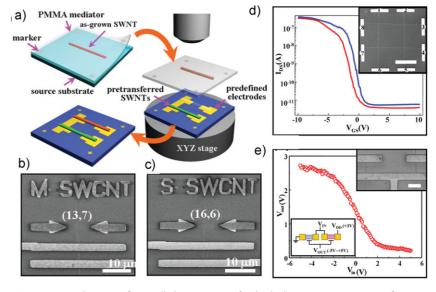


Figure 16. a) Schematic of controlled positioning of individual SWNTs on a target surface at a desired location, taking the fabrication of an inverter as an example. SEM images of b) a metallic tube and c) a semiconducting tube, each of which was placed onto electrodes marked with "M-SWCNT" and "S-SWCNT". d) Inset shows the SEM image of a 2  $\times$  2 SWNT crossbar circuit. Scale bar, 50  $\mu$ m. The red curve represents the  $I_{DS}-V_{GS}$  characteristic (at  $V_{DS}=0.1$ V) of two vertical semiconducting SWNTs measured with 3 and 4 as contacts, and the blue curve is that for nanotubes measured with 7 and 8 as contacts. e) Transfer characteristics of the inverter shown in the upper inset. The right tube is n-type while the left one is p-type. Scale bar, 10  $\mu$ m. The lower inset displays the schematic device configuration. Reproduced with permission from [118]. Copyright 2009, American Chemical Society.

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along tube axes. Then we focus on the typical electronic devices created from ultralong SWNT arrays, including FETs, diodes, memory and logic devices, and flexible devices.

### 5.1. Transport Properties of Ultralong SWNTs

The millimeter-long SWNTs have the same excellent length-normalized conductance  $^{[37,130]}$  and the same high mobility  $^{[133-135]}$  as short SWNTs. The limit of conductance for one SWNT is  $4e^2/h$  (where e is the elementary charge and h is the Plank constant,  $4e^2/h=155~\mu\text{S}$ , corresponding to a resistance of  $6.45~\text{k}\Omega)$ ,  $^{[3]}$  which is determined by the quantum conductance  $2e^2/h$  and the number of conducting channels (2 for one SWNT). Mobility ( $\mu$ ) is defined by the drift velocity of an electron or hole under a unit electric field. For a SWNT FET, mobility can be calculated as  $\mu=GL/ne$ , where G is the conductance, L the channel length, and n is the 1D carrier density. By substituting n as  $C_{\rm g}(V_{\rm th}-V_{\rm g})$ , mobility ( $\mu$ ) can be expressed as:  $^{[135]}$ 

$$\mu = \frac{L}{C_g} \frac{G}{V_{th} - V_g} \tag{1}$$

where  $C_{\rm g}$  is the gate capacitance per unit length,  $V_{\rm th}$  is the threshold gate voltage, and  $V_{\rm g}$  is the gate voltage. Since L, G,  $V_{\rm th}$ , and  $V_{\rm g}$  can be experimentally determined and  $C_{\rm g}$  can be calculated, finally mobility can be calculated.

#### 5.1.1. Length-Dependent Resistance in Ultralong-SWNT FETs

SWNT FETs with a channel length less than the mean free length ( $\sim\!1~\mu m$  or less) show ballistic transport;  $^{[132,136]}$  that is, the resistance approaches quantum resistance (6.45 k $\Omega$ ). For SWNT FETs with a channel length much longer than the mean free length, according to the diffusion model, the resistance should be scaled linearly to the length in the absence of any localized scattering.

Burke et al. measured the resistance of a 0.4 cm long semiconducting SWNT and compared it with the resistances of SWNT FETs with different channel lengths measured by different groups.<sup>[37]</sup> A linear relationship between the resistance and the channel length was found and the 1D resistance for SWNT FETs was estimated to be 6  $k\Omega~\mu m^{-1}$  , which indicated free scattering along the ultralong SWNTs. Kim et al. systematically measured the length-dependent resistance of SWNT FETs fabricated along the same individual SWNT with channel lengths from 200 nm to 400 µm. [130] They observed a similar drainsource current ( $I_{ds}$ ) to gate voltage ( $V_g$ ) curve at low drain–source voltage ( $V_{\rm ds}$ ) (<10 mV). At low length range (L < 100  $\mu$ m), the length-dependent resistance R(L) can be fitted by  $R(L) = \rho L + R_c$ , where  $\rho$  and  $R_c$  are interpreted as the 1D resistivity and contact resistance, respectively. This fitting gives  $\rho \sim 10 \,\mathrm{k}\Omega$   $\mu\mathrm{m}^{-1}$  and  $R_c \sim 8 \text{ k}\Omega$  at 300 K. The corresponding mean free length is  $\sim$ 0.65  $\mu m$ . Further resistance measurements at low temperature (4 K) give a typical  $\rho$  value of  $\sim$ 0.7–1 k $\Omega$   $\mu$ m<sup>-1</sup> and  $\sim$ 3–16 k $\Omega$ μm<sup>-1</sup> for metallic and semiconducting SWNTs, respectively, corresponding to mean free lengths of  $\sim$ 6–8  $\mu$ m and 0.4–2  $\mu$ m, respectively. At higher length range ( $L > 100 \,\mu\text{m}$ ), the resistance showed an exponential scaling to the length. This was attributed to unknown localized scattering.

### 5.1.2. Mobility Measurement in Ultralong-SWNT FETs

Mobility measurement for a 325  $\mu m$  long SWNT FET was carried out by Fuhrer's group.  $^{[135]}$  The maximum effective mobility  $\mu_{FE}$  was found to be  $79\,000\pm8000$  cm $^2$  V $^{-1}$  s $^{-1}$  at 300 K which was much larger than that for silicon FETs ( $\sim\!1000$  cm $^2$  V $^{-1}$  s $^{-1[137]}$ ). The mobility measured from ultralong SWNTs was larger and also more precise than that from short SWNTs ( $\sim\!9000$  cm $^2$  V $^{-1}$  s $^{-1[133]}$  or  $\sim\!3000$  cm $^2$  V $^{-1}$  s $^{-1[134]}$ ). In SWNT FETs with a short channel length, the contact resistance contributes a significant part to the total resistance of the device and the mobility is limited by the contact resistance.

### 5.2. Axial Band Structure Engineering of Ultralong SWNTs

The electrical transport properties of SWNTs are mainly determined by their energy band structures. For the ultralong, aligned SWNT arrays grown by conventional CVD techniques described in Section 2, the band structure is generally uniform along the tube axis for a specific tube. Experimentally it is also possible to modulate the local band structures along the tube axis for an ultralong SWNT by using various physical and chemical approaches. [24,25,128,129,138] Such kinds of axial band structure engineering of SWNTs may provide more possibilities for creating functional electronic and optoelectronic devices and for fabricating large-scale integrated circuits based on ultralong, aligned SWNT arrays.

The first successful example of the axial band structure engineering of SWNTs was demonstrated with the temperatureoscillation CVD approach by our group. [24,25] As described in Section 2, by dynamically modulating the growth temperature during the floating-mode CVD process, we have tuned the local tube diameters and hence the bandgaps of SWNTs, and created various intratube nanojunctions along the tube axis. Figure 17a-c exhibits the AFM image and the corresponding electrical characteristics of such an intratube nanojunction thus-grown. Rectifying behavior was clearly observed across this semiconductor-semiconductor intratube nanojunction with a rectification ratio of ca. 24.[24] The transfer characteristics showed that such kinds of intramolecular nanojunctions have higher on/off current ratios, reaching  $4.9 \times 10^5$ , than two segment tubes.<sup>[24]</sup> Currently, it is still difficult to control the exact location of the nanojunctions along the tube axis because of the difficulty of rapid temperature regulation. Great efforts are also needed to control the electronic properties (such as semiconductorsemiconductor, metal-semiconductor, and metal-metal) of the nanojunctions. Nevertheless, much space for further improvement still exists by introducing a more effective temperatureregulation mechanism together with the understanding of catalytic CVD processes.

The local band structure modulation of SWNTs can also be achieved by growing the ultralong tubes on heterogeneous or patterned substrates via floating-mode CVD. For example, on a trenched  ${\rm SiO_2/Si}$  substrate, the local band structures of a SWNT would be altered on the  ${\rm SiO_2-contacted}$  segments by van der Waals interactions. Our spatially resolved Raman spectroscopy studies demonstrated this possibility, as shown in Figure 17d and e.  $^{[138]}$  The Raman RBM and G-band showed obvious up-shifts in



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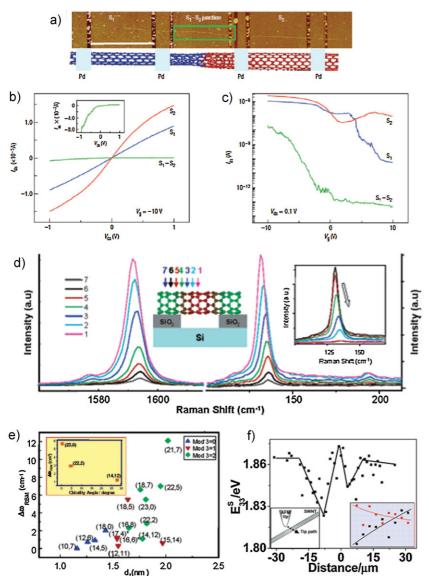


Figure 17. a) AFM image and schematic diagram of an SWNT with a semiconductor (S1)-semiconductor (S2) intratube nanojunction connected with four Pd electrodes. The scale bar is 4  $\mu$ m. b,c)  $I_{ds}$ – $V_{ds}$  and  $I_{ds}$ – $V_{gs}$  curves of the three SWNT segments shown in (a). The inset in (b) shows the rectifying behavior of the intramolecular junction. Reproduced with permission from [24]. Copyright 2007, Nature Publishing Group. d) Typical Raman G-band (left) and RBM (right) peak changes along tube axis as the laser spot moves from the middle of the trench to the SiO<sub>2</sub>-contacted region. The left inset exhibits the trench structure of the substrate with a nanotube, and the right inset shows the RBM spectra when the laser beam moves from the middle of the trench to the right side. e) Dependence of RBM peak shift on tube diameter and chirality, in reference to the suspended tube segment. Three types of symbols correspond to the SWNTs of  $(n-m) \mod 3 = 0$ ,  $(n-m) \mod 3 = 1$ , and  $(n-m) \mod 3 = 2$ , respectively. The inset is  $\Delta\omega_{RBM}$  versus the chiral angle for three SWNTs with similar diameter. Reproduced with permission from [138]. Copyright 2005, American Chemical Society. f)  $E_{33}^{S}$  along the SWNT axis after AFM manipulation. Left inset: schematic illustration of AFM manipulation on ultralong SWNTs. Right inset: the  $\Gamma$  value of 30 meV was obtained by fitting between experimental  $I_S$  and  $I_{AS}/I_{S}$  data and theoretical calculation. Reproduced with permission from [129]. Copyright 2007, American Chemical Society.

frequency ( $\omega_{RBM}$  and  $\omega_{G}$ , respectively) when the detecting laser beam was moved from the middle of the trench to the SiO<sub>2</sub> surface, along the tube axis (Fig. 17d). These spectral peak shifts are believed to originate from the surface-induced radial

deformation of SWNTs on the SiO2-contacted segments. The dependence of RBM peak shift on tube diameter and chirality, in reference to the suspended segment of tube, is summarized in Figure 17e. Generally the larger the tube diameter, the bigger the RBM peak shifts. The peak shift also seems dependent on the tube chirality. As seen from the inset of Figure 17e, the smaller the chiral angle, the bigger the RBM peak shifts.[138] These experimental observations are consistent with the previous theoretical prediction that the larger diameter tubes have greater deformations on a substrate surface. [139] From the intensity ratio of RBM anti-Stokes to Stokes peak, the shift of the interband transition energy ( $\Delta E_{ii}$ ) of SWNTs induced by radial deformation can be roughly estimated. [129] The  $\Delta E_{\rm ii}$  values fall into a range of 0-15 meV, and the shift direction seems related to the tube chirality. Similarly, instead of van der Waals interactions, localized charge transfer and/or chemical bonding between supporting substrate and SWNTs may also be utilized for the axial band structure engineering by growing on suitably designed patterned substrates.<sup>[138]</sup> The nanotransfer-printing techniques described in Section 4 will further extend this strategy to various substrates patterned with organic molecules, which are not tolerant of hightemperature growth conditions.<sup>[125]</sup> These potential approaches offer great freedom for tuning the local band structures of SWNTs.

Moreover, we also employed an AFM manipulation technique to tune the local electronic band structures of ultralong SWNTs by introducing localized strains. [128,129,140] We found that, under torsional strain, the electronic transition energy  $E_{\rm ii}$  variation of SWNTs followed a family pattern based on q=(n-m) mod 3: for semiconducting SWNTs,  $E_{33}^{\rm S}$  increased for q=+1,  $E_{33}^{\rm S}$  decreased and  $E_{22}^{\rm S}$  increased for q=-1, and for metallic SWNTs,  $E_{11}^{\rm M}$  always increased. As seen from Figure 17f, the  $E_{\rm ii}$  value shows continuous variation along the tube axis with AFM-induced torsional strains. [129]

### 5.3. Field-Effect Transistors and Diodes Based on Aligned SWNTs

Transistors and diodes are the basic components for electronic circuits. The FET is a basic logic device with three terminals used for

switching and amplification, and a diode is a two-terminal device used for rectification. FETs and diodes fabricated from aligned, ultralong SWNTs are essentially the same as those fabricated from short SWNTs. However, because it is attractive to integrate



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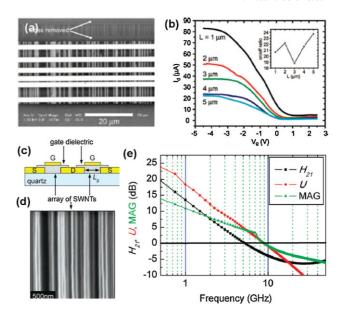
millions of devices along each ultralong SWNT, FETs and diodes based on ultralong SWNTs are investigated towards applications in integrated circuits.

### 5.3.1. FETs Based on Aligned, Ultralong SWNTs

SWNT-based FETs were first fabricated by Dekker and co-workers in 1998. [141] After that, SWNT FETs have been intensively investigated. There are two configurations of SWNT FETs: back gate and top gate. In the back-gate configuration, SWNTs are dispersed or directly grown on the silicon wafer with a  $\rm SiO_2$  layer, and then drain and source electrodes are fabricated on top of the SWNT. The  $\rm SiO_2$  layer serves as the dielectric and the back silicon can be used as the gate electrode. In order to get the high performance of SWNT FETs, it is convenient to reduce the thickness of dielectric and use high- $\kappa$  materials in transistors. The top-gate configuration has been widely used to meet this demand.

To reduce the device-to-device variations in performance caused by the uncertainty of chirality, one ideal approach is to fabricate chirality-specific SWNT FETs using one individual ultralong nanotube with an expected chirality. This has been realized by using the nanotransfer-printing technique developed in our group, as described in Section 4.3.[118] Another solution is to use densely packed, perfectly aligned arrays of non-overlapping linear SWNTs as the conduction channel. The multiple, parallel transport pathways in these arrays provide large current outputs and active areas, together with statistical averaging effects that lead to small device-to-device variations in properties. Rogers and co-workers demonstrated high on/off ratio, current output, and transconductance transistors by following this strategy. [57] The transistor they made involves as many as 2100 SWNTs, which revealed a device-level mobility and scaled transconductance approaching 1000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 3000 S m<sup>-1</sup>, respectively, together with a current output of up to 1 A in devices that used interdigitated electrodes. Similar high-current FETs have been fabricated by Liu and co-workers, as shown in Figure 18a and b. [69] With the specific growth technique, they succeeded in selectively growing dense and horizontally aligned semiconducting SWNTs on quartz. Such kinds of as-made SWNT FETs have an on/off current ratio up to 85. [69] Besides high current, another advantage of the FETs based on aligned SWNTs is the unique highfrequency performance. Rogers and co-workers constructed high-speed FETs from aligned arrays of hundreds of parallel nanotubes and assessed their performance by evaluating scattering parameters in the radio frequency (RF) range.[142] Such FET devices with sub-micrometer channel length showed unity current gain ( $f_t$ ) and unity power gain frequency ( $f_{max}$ ) as high as  $\sim$ 5 and  $\sim$ 9 GHz, respectively, with measured scattering parameters (S-parameters) that agree quantitatively with calculation (Fig. 18c–e). They pointed out that the elimination of metallic tubes is necessary for the application of aligned SWNTs in high speed electronics.

To fabricate SWNT-based CMOS devices, we need both p- and n-type SWNT FETs. Because of the oxygen doping effect, the as-prepared SWNT FETs are generally p-type FETs. Hence, it is essential to develop fabrication techniques for n-type SWNT FETs. Chemical doping of SWNTs is the general strategy for this purpose. Potassium<sup>[143–145]</sup> and PEI (polyethyleneimine)<sup>[146]</sup> have been frequently used as the dopants to convert p-type SWNT FETs



**Figure 18.** High on/off ratio FETs fabricated with as-grown aligned SWNTs array top-gated by solid electrolyte polymer films. a) SEM image of the devices. b)  $I_{\rm d}$ – $V_{\rm g}$  curves of the devices at  $V_{\rm ds}=80$  mV. Inset shows the on/off ratios obtained for the device as a function of the channel length. Reproduced with permission from [69]. Copyright 2009, American Chemical Society. c,d) Cross-sectional schematic illustration and SEM image, respectively, of radio frequency (RF) SWNT array transistors formed on a quartz substrate. e) Amplitude plots of RF SWNT array transistors for current gain ( $H_{21}$ ), unilateral power gain (U), and maximum available gain (MAG) for frequencies between 0.5 and 50 GHz. Reproduced with permission from [142]. Copyright 2009, American Chemical Society.

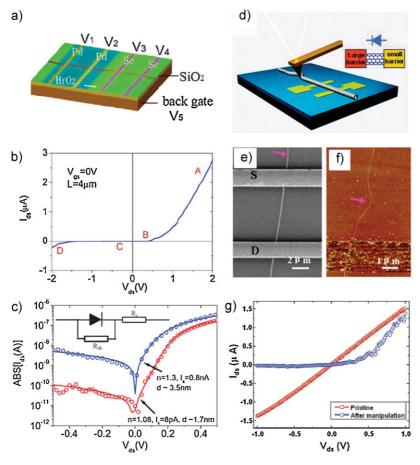
to the n-type. Annealing at vacuum or under inert gas was also proven to be effective for obtaining n-type FETs by eliminating the oxygen effect.<sup>[134,144]</sup> For the n-type SWNT FETs prepared by annealing, a layer of PMMA or gate oxide can be deposited on the SWNTs to keep these n-type FETs stable in air. [134,144] The Schottky barriers at the SWNT-electrode contacts usually dominate the transport properties of SWNT FETs. Metals with different work functions have been used to prepare both p-type  $^{[132,141,147]}$  and n-type SWNT FETs.  $^{[136,148-151]}$  While contact electrodes using high work function metals, like Pd,[132] Pt,[141] and Au, [147] yield p-type SWNT FETs, contact electrodes using low work function metals, like Ca<sup>[149]</sup> and Al,<sup>[148]</sup> yield n-type SWNT FETs. Recently, Peng and co-workers fabricated n-type FETs with ultralong SWNTs by using Sc as contacts. Such Sc-contacted SWNT FETs were air-stable and showed ballistic transport (the electron mean free length was ~190 nm at room temperature).[136]

### 5.3.2. Diodes Based on SWNTs

SWNT diodes were fabricated by using asymmetric gating <sup>[152,153]</sup> or asymmetric contacts. <sup>[151,154]</sup> Asymmetric gating and asymmetric contacts, which construct p–n-like junctions along SWNTs, limit electron injection only at one contact and hole injection only at the other contact and, hence, at forward bias, electrons and/or holes can be injected, while, at reverse bias, both



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**Figure 19.** a) Structure of an SWNT diode formed by a Pd contact and a Sc contact. b) The  $I_{\rm ds}-V_{\rm ds}$  curve of the diode in (a). c)  $I_{\rm ds}-V_{\rm ds}$  curves of two different SWNT diodes. Reproduced from [151]. d) Schematic illustration of how AFM manipulation introduces asymmetry in an SWNT diode. e) SEM image of an SWNT diode before AFM manipulation. f) AFM image of the SWNT diode after AFM manipulation. g)  $I_{\rm ds}-V_{\rm ds}$  curves of the SWNT diode before and after AFM manipulation. Reproduced with permission from [154]. Copyright 2008, American Chemical Society.

electrons and holes are blocked. Peng and co-workers fabricated almost ideal diodes along ultralong SWNTs by using Sc and Pd as contacts (Fig. 19a–c). At  $V_{\rm ds}>0.5\,\rm V$ , the device is on. The breakdown  $V_{\rm ds}$  is about  $-2\,\rm V$ . The ideality factor n (1.3 and 1.08 for SWNTs with  $d=3.5\,\rm nm$  and  $d=1.7\,\rm nm$ , respectively) was obtained by fitting the  $I_{\rm ds}-V_{\rm ds}$  curve using a modified diode equation:

$$I_{\rm ds} = \frac{V_{\rm ds} - IR_{\rm s}}{R_{\rm sh}} + I_{\rm s} \exp\left[\frac{q(V_{\rm ds} - IR_{\rm s})}{nk_{\rm B}T} - 1\right]$$
 (2)

where  $I_{\rm s}$  is the reverse saturation current,  $R_{\rm s}$  the effective series resistance,  $R_{\rm sh}$  the shunt resistance, T is the temperature,  $k_{\rm B}$  is the Boltzmann constant, q is the electron charge. Simply by using AFM manipulation, we created an asymmetric contact barrier in ultralong SWNT FETs, and obtained SWNT diodes (Fig. 19d–g). [154] The AFM tip stretched the SWNT near one contact to increase the Schottky barrier at the contact. As a result,

an air-stable SWNT diode with a high rectification ratio was obtained. Cutting the SWNT to reduce its contact length with one of two metal electrodes can also yield a SWNT diode device. The Schottky barrier at the manipulated SWNT–electrode was estimated to be  ${\sim}0.12\,\text{eV}.^{[154]}$ 

### 5.4. Memory and Logic Devices Based on Ultralong SWNTs

#### 5.4.1. Memory Devices Based on SWNTs

Memory devices based on SWNTs have been demonstrated by several groups.  $^{[63,133,155]}$  SWNT memory devices can be built based on the hysteresis in the  $I_{\rm ds}$ – $V_{\rm g}$  curve. [133,156] A positive (or negative)  $V_{\rm g}$  can be used to write a state, and a negative (or positive)  $V_{\rm g}$  can then be used to erase the state. The readout of the memory state can be done at zero  $V_{\rm g}$ . By using the merit of ultralong SWNTs, we designed a crossbar structure to achieve potential high-density memory arrays.<sup>[155]</sup> We also constructed a SWNT/ AgTCNQ@SWNT crossbar structure as a prototype memory, [155] in which an ultrathin AgTCNQ layer was electrochemically deposited onto the ultralong SWNT, followed by crossing over another ultralong SWNT. Excellent electrical bistability has been observed with such crossbar circuits.[155] This kind of crossbar device can be easily integrated into high-density memory arrays.

### 5.4.2. Logic Devices Based on SWNTs

In 2001, Dekker and co-workers fabricated a number of logic devices based on p-type SWNT FETs. [62] Since both p- and n-type SWNT FETs

with high performance can be fabricated, the natural idea is to integrate SWNT FETs into CMOS logic devices. As one of the basic logic devices, inverters have been fabricated from SWNTs. [118,134,144,148,157] Avouris and co-workers in IBM fabricated an inverter along the same SWNT for the first time with a gain of >1.[144] The low gain was attributed to the poor performance of back-gate configuration. Dai and co-workers employed a high-κ top-gate configuration and achieved a gain of  $\sim$ 60. [134] In the above inverters, n-type SWNT FETs were prepared by vacuum annealing followed by PMMA or gate oxide protection. Later, Peng and co-workers integrated an inverter from a Pd-contact p-type SWNT FET and a Sc-contact n-type SWNT FET along the same individual ultralong SWNT and achieved a gain of  $\sim$ 11. [157] The relatively high gain in this case was attributed to the ballistic transport performance achieved by using Pd and Sc as contact materials. The nanotransfer-printing technique described in Section 4 offers a powerful route for constructing logic devices. Using a PMMA thin film as the nanotransfer-printing mediator, we realized CMOS inverters with



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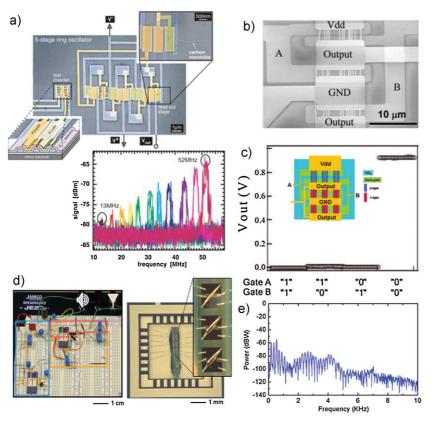


Figure 20. a) Structure of a ring oscillator integrated along an SWNT and its output characteristic. Reproduced with permission from [38]. Copyright 2006, AAAS. b,c) Defect-tolerant CMOS NOR with individual back-gated transistors. b) SEM image of CMOS NOR. c) Output characteristics of CMOS NOR. Inset: schematic diagram of CMOS NOR. Reproduced with permission from [159]. Copyright 2009, American Chemical Society. d,e) Circuit images and frequency response of a radio that uses carbon nanotube array transistors for all of the active components. d) Image of the radio with magnified views of SWNT transistors wire-bonded into DIP packages. e) Power spectrum of the radio output measured across a  $16\,\Omega$  load, recorded during a commercial broadcast of a traffic report. Reproduced with permission from [160]. Copyright 2008, American Academy of Science.

two parallel ultralong SWNTs, [118] in which the n-type FET was obtained by doping the SWNTs with PEI molecules. Millions of inverters can be fabricated in such a way along two parallel ultralong SWNTs without complex interconnects. Apparently, with an individual ultralong SWNT, "identical" p- or n-type FETs can be fabricated, which further leads to "identical" inverters. Integration of these "identical" inverters can yield highperformance SWNTs circuits. Such a strategy was first adopted by Avouris and co-workers.<sup>[38]</sup> As shown in Figure 20a, they integrated seven inverters along an individual ultralong SWNT,[38] in which one was for electrical transport test, one was for readout, and the remaining five were for the ring oscillator. Pd and Al were used as gate electrodes to obtain p- and n-type SWNT FETs, respectively. 13 and 52 MHz resonances were observed at  $V_{\rm dd} = 0.5$  and 0.92 V, respectively. This resonance frequency, limited by the parasitics, does not reach the limit of the intrinsic properties of SWNTs. Compared with the ring oscillators integrated from non-identical SWNT FETs, [62,158] the resonance frequency integrated from such "identical" inverters is 10<sup>5</sup>–10<sup>6</sup> times higher.

Reaping the benefits of technological progress related to aligned ultralong SWNTs, including wafer-scale synthesis, surfaceto-surface transfer, metallic tube removal and chemical doping, Zhou and his co-workers achieved remarkable progress with CMOSanalogous wafer-scale processing of integrated aligned SWNTs circuits.[159] In their work, the aligned SWNTs arrays were grown on 4 inch quartz or sapphire wafers via meticulous temperature control in a surface-directed CVD growth mode. The SWNTs arrays were then transferred onto 4 inch SiO<sub>2</sub>/Si wafers using gold film-mediated transfer-printing technique, followed by photolithographic implantation of metal electrodes and high-κ dielectrics.<sup>[159]</sup> Both top- and back-gated devices have been fabricated using conventional lithographic processes. To improve the on/off ratio of obtained devices, controlled electrical breakdown was used to remove metallic and high-leakage semiconducting nanotubes. The n-type FETs were fabricated by both chemical and electrostatic doping for constructing complementary electronics. Through these were troublesome processes, they finally constructed defect-immune PMOS and CMOS NOR and NAND circuits. Figure 20b and c demonstrates the CMOS logic circuits thus fabricated, which exhibit almost ideal performance with an output being close to 0 or 1.0 V.[159] Moreover, Rogers and co-workers made important progress in the practical implementation of SWNTs in high-speed analog circuits. [160] That group constructed RF analog electronic devices based on aligned SWNTs, such as narrow band amplifiers operating in the VHF band with power gains as high as 14 dB. As a demonstra-

tion, they fabricated a SWNT radio, in which the SWNT devices provide all of the key functions, including resonant antennas, fixed RF amplifiers, RF mixers, and audio amplifiers (Fig. 20d and e).

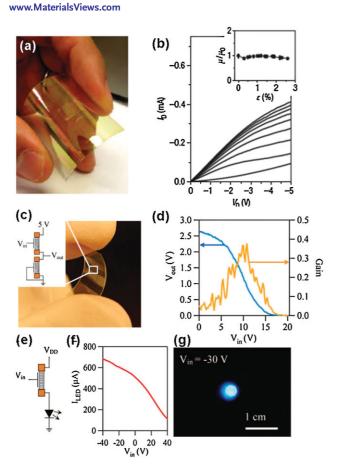
#### 5.5. Flexible Devices Based on Aligned SWNTs

SWNTs combine strength, flexibility, and high carrier mobility, a combination that open up a great opportunity for fabricating high-performance flexible electronic devices. [161] The low temperature of transfer-printing techniques introduced in Section  $4^{[110-114]}$  allows the fabrication of SWNT-based electronic devices on flexible plastics. Rogers and co-workers demonstrated a high-performance FET based on aligned SWNTs on a sheet of poly(ethylene terephthalate) (PET, 180 mm), where polyimide (1.6 mm) and indium tin oxide (ITO, 150 nm) provide the gate dielectric and gate, respectively (Fig. 21a). The linear-regime mobility, computed using a parallel-plate approximation for the capacitance, was estimated to be 480 cm²  $V^{-1}$  s $^{-1}$  (Fig. 21b). [57]



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**Figure 21.** a) Optical image of an array of SWNT transistors with aligned SWNTs on a flexible plastic substrate (PET). b) Current–voltage characteristics of a typical device on plastics. The inset shows the variation of the normalized mobility as a function of bending-induced strain. Reproduced with permission from [57]. Copyright 2007, Nature Publishing Group. c) Optical micrograph of fully transparent logic gates (inverters) on PET. The inset shows the circuit diagram of the PMOS inverter. d) Plots of  $V_{\rm out}$  (blue) and inverter gain (yellow, defined as  $dV_{\rm out}$  / $dV_{\rm in}$ ) versus  $V_{\rm in}$  of a fully transparent flexible PMOS inverter. e) The circuit diagram of an LED driven by a transparent SWNT transistor. f) Plot of the output current through the LED ( $I_{\rm LED}$  vs.  $V_{\rm in}$ ). g) Optical image of the LED under  $V_{\rm in}=30\,{\rm V}$ . Reproduced with permission from [162]. Copyright 2009, American Chemical Society.

Similar work was done by Liu and co-workers by selectively placing individual SWNTs on predefined electrodes on ITO/PET substrates using lift-off resist (LOR) as dielectrics. They concluded that the performance of FETs on plastics is comparable to that on conventional SiO<sub>2</sub>/Si substrates by comparing the transfer characteristics of the same SWNTs before and after transfer. Zhou and co-workers fabricated fully transparent devices based on aligned SWNTs on PET substrates using ITO as source, drain, and gate electrodes. The optical transmission of such flexible FETs was 80% in 350–1200 nm wavelength range. The device was bendable and the variations of transconductance and on-current were rather small with bending angles from 0° to 120°. They also fabricated fully transparent and flexible PMOS logic gates (inverters) on PET by using aligned SWNTs (Fig. 21c and d). The transparent FETs were used to control the GaN LED

with light intensity modulation of 10<sup>3</sup> as a proof-of-concept for future transparent displays (Fig. 21e–g).

Compared with the intense work on devices based on random and short tubes, studies on ultralong, aligned SWNT devices are still in the early stages. The known technical hurdles for the growth of such kinds of aligned, ultralong SWNTs, surface-to-surface transfer, and in situ removal of metallic tubes are the obvious reason for this status. Recent progress on these aspects will certainly accelerate research activities in this promising field.

### 6. Conclusions and Outlook

Aligned, ultralong SWNTs possess all the unique properties of SWNTs, such as high mobility, low resistivity, high current-carrying capacity, high thermal conductivity, high mechanical and chemical stabilities, and so on. The ultralong length and ordered 2D organization make them more suitable as the building blocks for future nanoelectronics. Moreover, segments of a SWNT with varied band structures could be obtained for multifunctional devices via axial band structure engineering.

In the last few years, the synthesis of aligned, ultralong SWNTs has been well-studied. The growth parameters, such as carbon source, catalyst, substrate, temperature, gas flow rate, and so on, have been systematically investigated. The length, density, and diameter distribution of SWNT arrays can be controlled to some extent. Wafer-scale, dense, and well-aligned SWNTs have become available by direct CVD synthesis. Identification and separation of semiconducting, ultralong SWNTs from metallic ones have also been extensively examined. Several efficient methods, such as plasma etching, irradiation, and covalent functionalization, have been developed or proven to be effective in the specific ultralong SWNT system for selectively removing metallic tubes or converting metallic tubes into semiconducting ones. Specific transfer-printing techniques are also developed to transfer the CVD-grown, ultralong SWNTs to desired substrates (e.g., wafers with electrode patterns or micro/nanostructures) for constructing functional architectures and devices. On the basis of these technical achievements, various electronic devices, such as FETs, diodes, memories, and logic circuits have been fabricated on both solid and flexible substrates with ultralong, aligned SWNTs. The high performance of these devices demonstrates their great potential in nanoelectronics. The capability of fabricating numerous FETs with identical performance on an individual ultralong tube offers the possibilities of constructing high-current FETs with fast switching performance and sensors with very high signal/noise ratio.

In spite of these progress points, great challenges still remain. The first and most troublesome issue is the chirality and diameter control of SWNTs during CVD growth. Better understanding of the decomposition reaction of the carbon source and function of catalysts and better control of the CVD process are undoubtedly crucial for further breakthrough. Without perfect control of tube chirality, one then needs to develop in situ separation techniques to remove metallic SWNTs from the mixed array. In fact, current techniques, such as plasma etching and light irradiation, also bring defects into the remaining semiconducting tubes, which lead to a sacrifice of device performance. Therefore, a practical



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nondestructive approach for electronic-type separation is needed. Moreover, although the transfer-printing techniques are effective for building complex and functional devices with ultralong SWNTs, they are inefficient and time-consuming, and further technical improvement is required. Besides, practical approaches for modulating the band structures of ultralong SWNTs and integrating large numbers of devices along the tube axis are highly desirable for generating integrated devices.

The research efforts on ultralong SWNT-based electronic devices are still at a very early stage. It should be noted that great progress has been achieved to date within a small number of years. Room still exists for efforts to be directed towards all the remaining technological challenges. There are two different targets for future SWNT-based device studies. The first target is to create beyond-silicon SWNT chips to compete with current silicon technology by making best use of the excellent performance of carbon nanotubes. The second target is to be complementary with the silicon technology. A wonderful example is the SWNT-based flexible and transparent devices. Such varieties of SWNT-based macroelectronics seem to be more promising at the present stage. In any case, effort and patience are needed

### Acknowledgements

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