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Aligned carbon nanotubes: from controlled synthesis to electronic applications

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Single-wall carbon nanotubes (SWNTs) possess superior geometrical, electronic, chemical, thermal, and mechanical properties and are very attractive for applications in electronic devices and circuits. To make this a reality, the nanotube orientation, density, diameter, electronic property, and even chirality should be well controlled. This Feature article focuses on recent achievements researchers have made on the controlled growth of horizontally aligned SWNTs and SWNT arrays on substrates and their electronic applications. Principles and strategies to control the morphology, structure, and properties of SWNTs are reviewed in detail. Furthermore, electrical properties of field-effect transistors fabricated on both individual SWNTs and aligned SWNT arrays are discussed. State-of-the-art electronic devices and circuits based on aligned SWNTs and SWNT arrays are also highlighted.

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1 Introduction

Silicon has dominated computing electronics since the demonstration of the first transistor in 1947. With the



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requirements of smaller and faster transistors, modern electronics have transistors with continuously increasing integration density and switching speed. However, the scaling-down process will soon reach the limit due to technological barriers in the fabrication processes and limitations in fundamental physics. As a result, researchers have been exploring new device structures and new semiconducting materials in order to continue this scaling-down process.¹ Carbon nanotubes (CNTs), especially single-wall carbon nanotubes (SWNTs), possess unique properties and are regarded as the landmark material in nanoscience and nanotechnology. The inherent small



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geometrical size of SWNTs of \sim 1 nm facilitates the fabrication of transistors down to nanoscale and optimizes the coupling between gate and channel. The ballistic transport of charger carriers with mean free paths on the order of microns in SWNTs renders them with intrinsic high charge carrier mobility as well as very high current density. Due to the absence of dangling bonds, SWNTs are chemically inert and stable. The good thermal conductivity of SWNTs is useful for effective heat and power dissipation in devices and circuits. Moreover, SWNTs are mechanically strong, and thin films of SWNTs have good transparency and flexibility. These unique properties lead to the fabrication of multifunctional and multipurpose devices and circuits with properties such as transparent, flexible, stretchable, bendable, etc. All these unique geometrical, electronic, chemical, thermal, and mechanical properties come together in SWNTs and make them a very attractive material for post-silicon era electronics.2-4

As a material with size down to nanoscale or even atomic scale, precisely and reproducibly structure-controlled preparation is vitally important for its fundamental studies and practical applications, and this is exactly the case for SWNTs. A SWNT can be conceptually regarded as a roll-up product of a graphene sheet, as illustrated in Fig. 1. The structure of a SWNT can be expressed with a pair of integers denoted as (n, m), *i.e.*, chirality, which determines the diameter and chiral angle of the SWNT. Each SWNT has a distinct geometrical structure, including diameter, chiral angle, length, and handedness,



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Fig. 1 Structures of SWNTs. (Left) Illustration of the roll-up of a graphene sheet to make a (6, 5) SWNT. (Right) Comparisons of SWNTs with different diameters, chiral angles, and lengths.

which depends on how it is rolled up. Theoretical and experimental studies have confirmed that electronic properties of SWNTs are determined by their geometrical structures.5-7 Among all (n, m) combinations, about 1/3 of SWNTs is metallic (n - m = 3q, where q is an integer) while the other 2/3 is semiconducting, possessing band gaps roughly inversely proportional to the nanotube diameters.⁵ As presented in Fig. 1, semiconducting (6, 5) and (13, 12) SWNTs possess the same infinite length and similar chiral angles, but with rather different diameters and thus different energy band gaps. In contrast, (6, 5) and (9, 0) SWNTs possess the same infinite length and similar diameters, but with different chiral angles and electronic structures, where (6, 5) SWNT is a semiconductor while (9, 0) SWNT is a metal. Even for the SWNTs with the same (6, 5) chirality, a change in their lengths will also lead to different properties and the importance of SWNT length increases significantly as it gets short.^{8,9} In a word, the structure of a SWNT determines it electronic, optical, thermal, and mechanical properties.¹⁰ Envisioning the attractive applications of SWNTs especially in electronics and optoelectronics, the ability to control their structures is of vital importance.¹

On the other hand, precise position and orientation control of SWNTs on substrates are important steps for their integration into electronic devices and circuits. Numerous efforts have also been devoted in recent years to control the morphology of SWNTs on the grown substrates. In this Feature article, we will review recent achievements on the controlled synthesis of horizontally aligned SWNTs and SWNT arrays, their electrical properties, and devices and circuits based on such well aligned, and structure and property well controlled SWNTs.

2 Controlled synthesis of aligned carbon nanotubes on substrates

2.1 Alignment control

Morphology control of nanotubes represents an important step towards the assembly of nanotubes from random tangled individuals into ordered structures^{11,12} and aligned arrays of SWNTs represent an advanced ordered structure of nanotubes. For the applications of nanotubes in electronics and integrated circuits, a prerequisite is to assemble individual building blocks into desired architectures with predefined locations and orientations. In this sense, horizontally aligned SWNT arrays represent one of the best candidates for nanotube electronics.

Several methods have been developed to grow aligned nanotubes, nanotube arrays, and complicated nanotube architectures on substrates in the past decade. Generally, the direction of nanotubes is determined by interactions between nanotubes and the environments, including substrates, gas flow, etc. External forces, for example, electric field and magnetic field, will also affect the growth direction of nanotubes.13-15 As early as 2001, electric field was applied to align nanotubes during the chemical vapor deposition (CVD) growth process by Dai and co-workers.13 Suspended and well aligned nanotubes were grown on substrates with the assistance of an electric field. The mechanism of nanotube alignment was attributed to the polarization of nanotubes under electric field and dipole moment induced alignment torques which can overcome the gas flow effect on the randomization of nanotube orientation.13 Later on, Joselevich and Lieber also demonstrated a similar process and further pointed out that such method may discriminate metallic and semiconducting nanotubes owing to their different behaviors in an electric field.14 Such electric-field assisted method was very recently used for the selective growth of metallic-enriched nanotubes by Zhang et al.16 The disadvantages of these methods are that electric field and patterned electrodes are used, which brings difficulty to the experiments. Meanwhile, the length and the linear density of aligned nanotubes are low. Nevertheless, these studies represent the very initial attempts on the growth of well aligned nanotubes on the surface and stimulate further studies.

Later on, gas flow was found to be an effective force to align nanotubes during CVD growth. Liu and co-workers invented a fast heating process to grow long and horizontally aligned SWNTs on SiO₂/Si substrates, as can be seen from the scanning electron microscopy (SEM) image in Fig. 2a.17 In their method, substrates loaded with catalysts were transferred to the high temperature zone quickly, where the sudden change of catalyst environment leads to the floating of nanotubes into a fast-flow region and the wind of the flowing gas aligns the nanotubes via the tip growth mechanism.¹⁷⁻¹⁹ This process resembles kites flying in sky. In such a process, the alignment direction of nanotubes is determined by the gas flow direction. Further understanding and modifications of the flow direct mechanism lead to better nanotubes in terms of perfection of nanotube alignment and linear density of as grown SWNTs (Fig. 2b).20-23 It has also been demonstrated that the fast heating procedure is not a must for growing aligned ultralong nanotubes. For example, ethanol carbon source was reported to grow aligned gas-directed nanotubes without the fast heating procedure and it was believed that carbon source may play an important role in the growth of ultralong and aligned SWNTs.^{24,25} Nevertheless, the growth of aligned long SWNTs was also reported by using methane as carbon source.26 Another report showed that making catalysts stay at a higher position than the substrates benefits the growth of aligned long SWNTs.27 Gas flow directed grown nanotubes can have lengths up to several millimeters



Fig. 2 Gas flow mediated growth of aligned long CNTs. (a) Fast heating method.¹⁷ Adapted from ref. 17 with permission. Copyright 2003 American Chemical Society. (b) Low gas feed rate.²¹ Adapted from ref. 21 with permission. Copyright 2009 American Chemical Society. (c) Centimeter long CNTs.²⁸ Adapted from ref. 28 with permission. Copyright 2010 Wiley. (d) 2D SWNT networks by multiple growth.³⁴ Adapted from ref. 34 with permission. Copyright 2003 Wiley. (e) Aligned SWNTs across a trench on substrates.²⁷ Adapted from ref. 27 with permission. Copyright 2006 American Chemical Society.

and, more recently, up to tens of centimeters, as reported by Wei and co-workers and Li and co-workers (Fig. 2c).^{25,28-30} The growth mechanism and kinetics of ultralong SWNTs by gas mediated growth were studied.31-33 Based on this understanding, two dimensional networks of nanotubes with arbitrary angles have been grown by multiple growth where the relative orientation between substrates and gas flow was changed (Fig. 2d).³⁴ Meanwhile, the growth of more complicated serpentine nanotubes has been reported by Joselevich and co-workers.35 Another feature of gas mediated growth is that nanotubes can grow across trenches on substrates,²⁷ this is evidence showing that the nanotubes grow in the gas phase and float during the process, the so-called kite mechanism. Therefore, this method is very suitable for the direct growth of suspended and ultraclean nanotubes (Fig. 2e), from which the intrinsic properties of nanotubes and the effect of substrates on properties nanotubes be the of can examined experimentally.36-43

Gas mediated growth represents a significant advance for the growth of ultralong, clean, and suspended nanotubes and provides material platforms to study the electronic and optical properties of individual nanotubes. However, the linear density of nanotubes grown from this method is typically low, for example, <0.1 SWNT per micron. This limits their applications in electronic devices due to the low drive current. In addition, nanotube alignment by gas flow is not perfect and some cross-over happens. In this regard, perfectly aligned and high density nanotube arrays are highly desired. Through 2004 to 2005, several groups, including ours, have discovered the growth of high density aligned nanotube arrays on single crystalline

substrates, including sapphire (Al₂O₃),^{44,45} quartz (SiO₂),⁴⁶ magnesium oxide (MgO),47 silicon,48 etc. Two mechanisms were proposed to understand why nanotubes preferentially align along specific orientations on such substrates, *i.e.*, step-edge induced alignment (Fig. 3a and b) and crystalline orientation (Fig. 3c and d) induced alignment. Plenty of experimental and theoretical studies have been performed to compare the two alignment mechanisms.⁴⁹⁻⁵² For aligned nanotubes growth on such single crystal substrates, a high temperature air anneal was found to be important to improve the degree of nanotube alignment. Catalysts were typically patterned as stripes and well aligned, high density nanotube arrays can be grown within adjacent stripes. The dependence of nanotube alignment on different crystalline facets has been extensively studied and ST cut and Y cut quartz are now most commonly used, which give the best nanotube alignment as can be seen from SEM and atomic force microscopy (AFM) characterization (Fig. 3e and f).44,47,48,53-56 Compared to the gas flow mediated aligned growth of nanotubes, crystalline wafers give much higher density, up to 10 SWNTs per micron, which is more than 100 times higher than the gas flow aligned SWNT arrays. On the other hand, it is typically believed that nanotubes have a strong interaction with underneath crystalline substrates and stay on substrates during the growth process. The lengths of nanotubes grown using crystalline substrates are typically shorter (tens to hundreds of microns) than gas flow aligned nanotubes.57

By combining different nanotube alignment methods, *i.e.*, gas flow alignment and crystalline substrate alignment, 2D architectures of nanotubes can be fabricated easily in a more rational and controllable fashion. For instance, Zhang, Liu and co-workers have reported rational growth of serpentine nanotubes on quartz and one step growth of 2D nanotube networks.^{58,59}

Despite the fact that aligned SWNTs grown on crystalline substrates, especially quartz, have a pretty high density compared with gas flow mediated SWNT arrays, it still needs to be further increased to merit some applications. For example, for electronic applications of nanotubes, the drive current and transconductance are important figures of merit, and both of which could increase by increasing the nanotube linear density. Therefore, lots of efforts have been devoted to further increase the linear density of aligned SWNT arrays, including improvements of growth recipe,60 multiple cycle growth61,62 and multiple cycle transfer.^{63,64} For example, we have developed a low pressure CVD process combined with stacked transfer using Au films, and nanotubes with a linear density >50 SWNTs per micron have been achieved (Fig. 4).63 FETs fabricated using these ultrahigh density SWNT arrays offer the highest normalized on current density and transconductance, which will be discussed in detail later.

2.2 Diameter control

The band gaps of semiconducting SWNTs are directly related to their diameters. Also, diameters of nanotubes play an important role in metal electrode–nanotube contact type and resistance. Therefore, diameter control is very important for the application of nanotubes in electronics. A clear understanding of the



Fig. 3 Crystalline substrate guided growth of aligned SWNT arrays. (a and b) Scheme of the edge steps on sapphire substrates and AFM image of the as grown aligned SWNTs.⁴⁵ Adapted from ref. 45 with permission. Copyright 2004 Wiley. (c and d) Atomic illustration of a SWNT aligning on the *a*-plane sapphire substrate and the corresponding AFM image.⁴⁴ Adapted from ref. 44 with permission. Copyright 2005 American Chemical Society. (e and f) SEM and AFM images of aligned SWNT arrays on the quartz substrate.⁵⁴ Adapted from ref. 54 with permission. Copyright 2006 American Chemical Society.



Fig. 4 Density improvements of aligned SWNT arrays. (a) Schematic of stacked transfer of CVD grown aligned SWNT arrays on quartz. (b) SEM image of as grown SWNT arrays on quartz. (c–e) SEM images of transferred SWNT arrays on SiO₂/Si substrates with one time, two time, and four-time transfer. The nanotube linear density reaches 55 SWNTs per micron after four-time stacked transfer.⁶³ Adapted from ref. 63 with permission. Copyright 2009 Springer.

catalyst size–CNT diameter relationship is the first step towards the diameter controlled synthesis of SWNTs. It is generally considered that the diameters of as grown SWNTs are strongly related to the sizes of catalyst nanoparticles which are used for

SWNT synthesis based on transmission electron microscopy (TEM) observations (Fig. 5a-c).65 In real cases, however, the shape of nanoparticles may be irregular, especially during the high temperature nanotube growth process (Fig. 5d),⁶⁶ which makes it difficult to accurately define the relationship between the diameters of CNTs and the sizes of catalyst nanoparticles which they grown from. Nevertheless, it is still safe to conclude that the size of nanoparticles sets the upper boundary for the diameter of nanotubes.67 Meanwhile, the morphologies and atomic steps on catalyst particles may have effects on the growth of nanotubes.68 Therefore, how to control the sizes and morphologies of nanoparticles becomes a key issue. Numerous efforts have been devoted to synthesis of nanoparticles with uniform sizes, aiming at growing nanotubes with unique diameters (Fig. 5e).65,69-73 However, the diameters of nanotubes still have a pretty broad distribution in real samples even with uniform catalysts used. This is because many factors may influence the sizes and morphologies of nanoparticles, consequently the structures of as grown nanotubes. These factors include chemical composition of nanoparticles, growth temperature, gas composition, substrates, etc. For example, nanoparticles may migrate and aggregate with each other, especially on flat surfaces, leading to an increase in their sizes. On the other hand, high temperature catalyst vaporization or diffusion into the substrate leads to a decrease in nanoparticle sizes. How the nanoparticle sizes will change in a specific condition is jointly determined by many factors like growth temperatures and the interaction strength between catalyst nanoparticles and substrates or supports. The competing of many of these factors makes it extremely difficult to precisely control the sizes and morphologies of tiny catalyst nanoparticles. Nevertheless, by carefully controlling the growth recipe, narrower and narrower diameter distributed SWNTs have been grown. For example, Ago and co-workers show recently that controlled vacuum annealing leads to 76% of



Fig. 5 Diameter control of nanotubes. (a–c) TEM images show the growth of SWNTs from discrete catalyst nanoparticles and the SWNT diameter–nanoparticle size relationship.⁶⁵ Adapted from ref. 65 with permission. Copyright 2001 American Chemical Society. (d) High resolution TEM image shows the nucleation of a SWNT cap from a Fe₃C nanoparticle.⁶⁶ Adapted from ref. 66 with permission. Copyright 2008 American Chemical Society. (e) Structure of a Fe₃₀Mo₈₄ cluster which has a defined amount of atoms and size.^{69,106} Adapted from ref. 106 with permission. Copyright 2004 Materials Research Society. (f and g) Narrow diameter distributed aligned SWNT arrays grown on sapphire by controlled vacuum annealing.⁷⁴ Adapted from ref. 74 with permission. Copyright 2011 American Chemical Society.

SWNTs having diameters within 1.3–1.4 nm in horizontally aligned SWNT arrays grown on sapphire (Fig. 5f and g).⁷⁴

In addition to the idea of starting with size-uniform catalyst nanoparticles, how to minimize the size and morphology change of nanoparticles during the CVD growth process is another important strategy. Generally, SWNTs grown on flat substrates have relatively large diameters and broad diameter distributions compared with those grown on porous material supported catalysts. This may relate to the fact that large surface area porous supports prevent nanoparticles from aggregation and stabilize small nanoparticles for SWNT growth with small diameters and narrow diameter distributions.75 It is also reported that an epitaxial relationship between catalyst nanoparticles and crystalline substrates prevents nanoparticles from aggregation, thereby leading to nanotube products with a narrow diameter and chirality distribution.76 The reduced growth temperature should also be beneficial for the growth of narrow diameter distributed SWNTs since this will mitigate variations in nanoparticle sizes and morphologies.77

Another strategy is to choose those catalysts with excellent high temperature stability, *i.e.*, high melting points and low saturated vapor pressure, as this will also reduce their structural fluctuation in the high temperature nanotube growth environment and thus is beneficial for the diameter-controlled growth of SWNTs. Historically, iron group metals (Fe, Co, Ni) and their alloys are the major catalysts for SWNT growth. It has been shown in the past few years that high quality SWNTs can also be grown from metals other than iron group ones, nonmetal oxides, as well as carbon species.⁷⁸⁻⁹² These discoveries demonstrated that carbon solubility and catalytic decomposition of carbon sources are not a must to determine whether a particle can grow SWNTs or not. It has been suggested by Homma and co-workers that nano-sized particles only serve as templates to help the initial nucleation of nanotube caps.⁸⁸ These findings greatly expand the knowledge of the function of catalysts for nanotube growth. Moreover, they open up a novel angle to reveal the growth mechanism of SWNTs and provide opportunities for the diameter and even chirality control *via* catalyst engineering. For example, it has been reported that SiO₂ nanoparticles, which have a much higher melting point and lower saturated vapor pressure than iron group metals,⁹³ can grow nanotubes with relatively narrow diameter distribution⁹¹ *via* a vapor–solid–solid mechanism.⁸⁵ In addition, fullerenes have been reported to grow SWNTs with discrete diameter distributions, rather than continuous distribution from other catalyst systems.^{94,95}

It has also been reported in the literature that a large amount of experimental parameters, including catalyst pretreatment,⁹⁶ growth temperatures,^{97–99} gas pressure,¹⁰⁰ substrates,¹⁰¹ gas composition and flow rates,^{102,103} dopants,^{104,105} also have effects on the diameter distributions of as produced SWNTs. Highly likely, the common underlying mechanism for these observations is that the sizes and morphologies of catalyst nanoparticles may change under different conditions. Another possibility is that under different growth conditions, different small fractions of nanoparticles were "selectively" activated and, consequently, different growth conditions grow different nanotubes even though using the same set of catalysts.¹⁰³

2.3 Electronic property control

SWNTs can be either metallic or semiconducting, depending on their chiralities. Semiconducting SWNTs can be used as active

channel materials in electronic devices and circuits, while the presence of metallic SWNTs may lead to short circuit since they cannot be turned off. Consequently, metallic and semiconducting controlled synthesis is another big challenge, probably the most important one at this moment, for the application of nanotubes in electronics, especially digital electronics and circuits where high on/off ratios are required. Since semiconducting SWNTs are more attractive for device applications, most of the efforts have been devoted to the selective synthesis of semiconducting-enriched SWNTs.

It has been reported by Dai and co-workers that remote plasma-enhanced CVD (PECVD) is capable to grow semiconducting enriched SWNTs, as measured in a nanotube fieldeffect transistor (FET) configuration (Fig. 6a).¹⁰⁷ The preferential growth of semiconducting SWNTs was suggested to originate from the thermodynamic stability differences between semiconducting and metallic SWNTs, especially in the small diameter region.¹⁰⁸ It has been reported that PECVD can also selectively grow semiconducting enriched SWNTs in a vertical forest.¹⁰⁹ However, the detailed mechanism and the function of plasma are not well understood. A more recent study shows that abundant metallic SWNTs are still present in the PECVD grown samples as evidenced by Raman spectroscopy.110 However, such metallic SWNTs are very defective due to irradiation damage in the PECVD process, thus opening a band gap in those metallic SWNTs and showing semiconducting behavior. Therefore, the quality of PECVD grown SWNTs may be not very high.

It has been shown that metallic SWNTs are more reactive than their semiconducting counterparts in many chemical reactions.¹¹¹⁻¹¹³ Therefore, selective suppression of the nucleation or etching away metallic SWNTs should be a rational strategy to selectively grow semiconducting SWNTs. Zhang, Liu, and co-workers have shown that introducing a UV light into a CVD furnace leads to the preferential growth of semiconducting SWNTs (Fig. 6b).¹¹⁴ UV light is thought to prevent the nucleation of metallic SWNTs selectively, thereby leading to the growth of semiconducting SWNTs with decreased density. Another interesting report from Liu, Li, and co-workers demonstrated that addition of methanol in an ethanol carbon source helps to grow semiconducting-enriched SNWTs.⁵⁷ The selective growth of semiconducting SWNTs was verified by multiple laser Raman and electrical transport measurements (Fig. 6c–e).¹¹⁵ They further proposed that high concentration of OH radicals produced from methanol will selectively etch away metallic SWNTs due to their small ionization energy. The use of quartz substrates was also found to be important for the selective growth of semiconducting SWNTs in this process.⁵⁷

Our group recently discovered that by simply switching carbon source from ethanol to isopropanol, wafer scale semiconducting-enriched SWNT arrays can be grown (Fig. 7),¹¹⁶ which was also reported by Wong and co-workers.¹¹⁷ The preferential growth of semiconducting SWNTs was verified by multiple laser Raman spectra and individual and aligned SWNT array FETs. Based on the individual SWNT FET measurement, we found that more than 90% of SWNTs are semiconducting. The absence of external energy like plasma or UV light as well as the use of single carbon source simplify the process and make it more robust. Mass spectroscopic analysis shows that the isopropanol CVD process has a relatively high concentration ratio of water to carbon species, which may be responsible for the selective growth behavior since water vapor has been reported to selectively etch away metallic SWNTs.¹¹⁸

There are two possible mechanisms which may account for the selective growth of semiconducting SWNTs. One is that selectivity happens during the initial nucleation periods, *i.e.*, the nucleation of metallic SWNTs is somehow prohibited. Another one is selectivity happens after SWNT nucleation, *i.e.*, both metallic and semiconducting SWNTs are nucleated and grown, but later on the metallic SWNTs will be etched away *in situ* due to their high reactivity. To study this, we chose density gradient ultracentrifugation separated high purity semiconducting and metallic SWNTs and to study whether such



Fig. 6 Methods for the selective growth of semiconducting enriched SWNTs. (a) PECVD setup.^{107,108} Adapted from ref. 107 with permission. Copyright 2004 American Chemical Society. (b) UV light assisted CVD setup.¹¹⁴ Adapted from ref. 114 with permission. Copyright 2009 American Chemical Society. (c–e) SEM image and laser Raman spectra of semiconducting-enriched SWNT arrays grown from ethanol and methanol mixed carbon sources.¹¹⁵ Adapted from ref. 115 with permission. Copyright 2009 American Chemical Society.



Fig. 7 Wafer scale growth of semiconducting SWNT arrays using isopropanol as carbon source. (a) Optical images of a four inch wafer with aligned SWNT arrays grown on. (b) SEM image of aligned SWNT arrays. (c–f) Raman spectra comparisons of ethanol-grown and isopropanol-grown SWNTs under different excitation lasers.¹¹⁶ Adapted from ref. 116 with permission. Copyright 2012 American Chemical Society.

already-formed SWNTs will show any difference during the isopropanol CVD process. The results show that neither metallic nor semiconducting SWNTs were reacted at 900 °C under the isopropanol CVD environment,¹¹⁶ thus suggesting that the selectivity should happen during the initial SWNT nucleation period, rather than post-growth selective etching.

In addition to the above methods, element doping was also reported to be able to modify the electronic properties of SWNTs.¹¹⁹⁻¹²² For example, it has been theoretically predicted by Wang, Bai, and co-workers that boron and nitrogen co-doping will open up energy band gaps in metallic SWNTs and convert them into semiconductors.¹¹⁹ Electrical transport measurement on SWNT arrays verifies this predication. It has also been calculated that how the electronic structures of SWNTs will change depends very sensitively on the types of doping (local chemical bonds of the dopants) as well as doping concentration.¹⁰ Consequently, one major challenge for this approach is how to precisely control and identify the doping type and concentration.

Another attractive strategy to obtain semiconductingenriched SWNT arrays is post-growth wafer-scale separation. This still utilizes the reactivity difference between metallic nanotubes and semiconducting ones.111 Several methods have been demonstrated to fulfill the wafer scale treatment of nanotubes towards removing metallic ones.113,123,124 For example, CH₄ plasma was used to selectively etch away metallic SWNTs from their semiconducting counterpart.¹¹³ In addition, it has been reported that light irradiation may convert metallic SWNTs into semiconducting ones via chemical fictionalization¹²⁴ or etch away metallic SWNTs,¹²⁵ depending on the specific experimental conditions. Water vapor was also found to selectively etch away metallic SWNTs.118,126 In addition, Zhang et al. recently reported that by simply sonicating the as grown aligned SWNTs in aqueous solution of surfactant, metallic SWNTs were selectively removed.127 These approaches, especially those can be conducted on a wafer scale, represent an

important alternative to solve the electronic heterogeneous problem of SWNTs. Some problems within these approaches are the separation efficiency and how to avoid damage to the electronic properties of the remaining semiconducting SWNTs.

Due to the high potential of semiconducting nanotubes in nanoelectronics and macroelectronics, it is more attractive to selectively synthesize semiconducting SWNTs. Moreover, the relatively high reactivity of metallic SWNTs makes it inherently less difficult to selectively grow semiconducting SWNTs by adding additional etching species.¹²⁸ Nevertheless, there are still few studies which show that metallic SWNT enriched samples can be selectively grown.^{68,129,130} One study shows that gas composition during catalyst pretreatment leads to different morphologies of catalyst nanoparticles, which may account for the selective growth of metallic SWNTs.⁶⁸ However, the reason why metallic SWNTs can be selectively grown remains largely intact as compared with our understanding on the selective growth mechanism of semiconducting SWNTs.

2.4 Chirality control

Chirality-controlled synthesis of SWNTs is the holy grail of the nanotube synthesis community and is one of the most challenging directions. It is generally believed that the chirality of a SWNT will be fixed during the initial nucleation stage and the follow up steady growth stage will not change its chirality, just extending its length. This is supported by the fact that ultralong SWNTs typically possess the same chirality along their lengths¹³¹ unless the growth condition changes.⁹⁷ Therefore, deep understanding of the nucleation events and nucleation control is critical to fulfill the chirality control of SWNTs. Abundant theoretical calculations have been performed to understand the nucleation possibilities of different chirality SWNTs based on thermodynamic considerations. From the thermodynamic point-of-view, it is argued that certain types of SWNTs are more stable and require less energy to form than the

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others, thus are more abundant in products. Several theoretical calculations support this argument based on the epitaxial relationship between catalyst particles/surfaces and SWNT nuclei.132-134 Experimentally, many factors were identified to have effects on the chirality distribution of SWNTs, including catalysts and catalyst supports, growth temperatures, gas pressure, substrates, etc. 53,76,100,135-148 In real SWNT samples, they typically have broad chirality distributions, but not featureless distributions. Indeed, certain chiralities of SWNTs, like (6, 5), (7, 6), (7, 5), (8, 4), (9, 8), (13, 12), were found to be present more from than others many different synthesis methods.^{75,135,137,143-145,147} This shows certain degree of consistency with the thermodynamic arguments that these nuclei may be more stable than the others.

The stability of metal catalyst nanoparticles at high temperature may have a paramount effect on the chirality controlled growth of SWNTs. Theoretical calculations suggested that different metals or different crystalline facets of the same metal can lead to the selective nucleation of specific SWNT nuclei, and consequently, chirality controlled growth of SWNTs. However, SWNTs are grown at high temperatures, typically around 800-900 °C in the CVD process and ranging widely from 400 °C to several thousand Celsius degrees in CVD, arc discharge, and laser ablating processes. In such high temperatures, the nanoparticles may become (quasi) melting or the outmost surface of the catalyst nanoparticles will become (quasi) melting and highly mobile. For example, in situ TEM observations show structural fluctuations of metal nanoparticles during the nanotube growth process.66 Consequently, the possible epitaxial relationship between SWNT nuclei and catalyst surfaces will disappear and there will be no chirality-dependent nucleation behavior. To enhance the modulation of catalyst sizes, structures, and properties to the diameters and chiralities of as grown SWNTs, it is critically important to select catalysts with excellent high temperature stabilities. One choice is the use of high melting point elements as catalysts for SWNT growth. Another choice is the use of nonmetal species, which usually have higher melting points than Fe, Co, and Ni, as catalysts.78-81,84,85,87,140,149 We believe that crystalline nanoparticles should be better than amorphous ones due to the possible epitaxial relationship between nanoparticles and SWNT nuclei. Current experimental results show that by careful design and selection of catalysts, the chirality distribution of SWNTs can be narrowed and few kinds of chiralities can be selectively grown. Nevertheless, it is still far away for single chirality control.

An alternative strategy is to use short SWNTs to template further SWNT growth, aiming at single chirality controlled synthesis. As shown in Fig. 8a, Smalley, Tour, and co-workers docked Fe nanoparticles at the ends of short SWNT segments for the so-called amplification growth.¹⁵⁰ AFM analysis (Fig. 8b and c) shows that the amplified materials have nearly the same diameter and alignment orientation compared with short SWNT templates. However, whether the original chirality of SWNTs preserved or not is unknown. Later on, Zhang, Liu, and co-workers reported the cloning growth of SWNTs using short SWNT segments (Fig. 8e–l).¹⁵¹ In their method, they used ebeam lithography to cut CVD grown long SWNTs into short segments and directly used these segments, without the

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Fig. 8 Chirality-controlled growth of SWNTs by nanotube amplification and cloning. (a–c) SWNT amplification process. (a) Schematic of SWNT ends being docked by metal nanoparticles and nanotube amplification under C₂H₄. (b and c) AFM images of the short SWNT (b) and its amplification material (c).¹⁵⁰ Adapted from ref. 150 with permission. Copyright 2006 American Chemical Society. (d–l) SWNT cloning using short nanotube segments. (d–f) Schematic of long SWNTs being cut by e-beam lithography and the nanotube cloning process. (g–l) SEM and AFM images of original SWNTs before cutting (g and h), after cutting (i and j), and after cloning growth (k and l).¹⁵¹ Adapted from ref. 151 with permission. Copyright 2009 American Chemical Society.

necessity of docking metal nanoparticles, for the second growth of SWNTs. AFM and Raman characterization shows that the newly grown segments have the same diameter and RBM position compared with the original seeds. They further suggest that the newly grown SWNTs have the same chirality compared with the short SWNT seeds.

The SWNT amplification and cloning growth concepts demonstrate the possibility of SWNT lengthening directly from short SWNT segments and represent a significant success towards the chirality controlled growth of SWNTs.^{150,151} In these methods, short segments of SWNTs have random chiralities, and consequently, the finally grown SWNTs are supposed to have many chiralities. On the other hand, in recent years, single chirality SWNT separation methods have become available. For example, DNA based molecule recognition and separation has been developed by Zheng and co-workers which is able to separate single chirality SWNTs with exemplary high purity, *e.g.*, higher than 90%.¹⁵² Therefore, it would be intriguing to combine SWNT separation technologies with selective growth, aiming at solving the SWNT chirality problem.

Recently, we have developed such an approach, named vapor phase epitaxy (VPE) growth, which used chirality preselected SWNTs as seeds, to realize the chirality controlled growth of both

semiconducting (6, 5) and (7, 6) SWNTs as well as metallic (7, 7) SWNTs (Fig. 9).¹⁵³ In our process, single chirality SWNT seeds with purity up to 90% or even higher were first separated by the DNA based nanotube separation method.¹⁵² Then, the DNA wrapped nanotube seeds were dispersed on quartz or SiO₂/Si substrates and underwent a three step pretreatment process, including air annealing, water annealing, and hydrogen annealing. Finally, methane or ethanol was introduced to initiate the nanotube VPE growth at 900 °C. AFM shows that the average lengths of SWNTs increased from around 300 nm to more than 30 μ m after the VPE process for (7, 6) nanotubes, suggesting that short SWNTs indeed grow longer. Raman spectra under multiple lasers show that the VPE grown SWNTs have the same RBM position compared with the original nanotube seeds for all chiralities we tested. Here we emphasize that for small diameter nanotubes like (6, 5), (7, 6), and (7, 7), Raman characterization is precise and unambiguous to determine their chiralities since adjacent nanotubes have distinct electron transition energies. Our electrical measurements using single nanotube FETs also demonstrate the semiconducting behavior of cloned (6, 5) and (7, 6) SWNTs, as will be discussed later.

The above experiments of chirality-controlled SWNT growth from short SWNT seeds demonstrate the possibility of nanotube extension from short segments. Therefore, synthesizing different chirality nanotube seeds (or the cap structures) becomes very important and there are recently many exciting progress on this



Fig. 9 Chirality-controlled synthesis of SWNTs by the VPE approach. (a–d) AFM images of DNA separated single chirality SWNT seeds before (a) and after (b–d) VPE growth. The average lengths of SWNT seeds and VPE grown SWNTs are 300 nm and 34.5 μ m, respectively. (e–g) SEM images of VPE grown SWNTs on SiO2/Si and quartz substrates. (h–j) Raman spectra of (7, 6) seeds (h), VPE grown (7, 6) SWNTs (i), and Raman spectra along a long VPE grown (7, 6) SWNT (j).¹⁵³ Adapted from ref. 153 with permission. Copyright 2012 Nature Publication Group.

direction.^{154–158} For example, Scott and co-workers have reported chemical synthesis of a $C_{50}H_{10}$ molecule, which has exactly the same structure with the end cap plus a short segment of a (5, 5) nanotube.¹⁵⁸ The successful bottom up synthesis of such molecule precursors expands the availability of different nanotube seeds, which eventually may lead to the chirality controlled synthesis of many single chirality SWNT species.

In addition to the thermodynamic governed chiralitydependent nanotube nucleation, another important factor which has only very recently been realized is the kinetic aspect, *i.e.*, chirality-dependent growth rate of SWNTs.¹⁵⁹ It is proposed by Yakobson, Ding, and co-workers that the growth rates of SWNTs are proportional to their chiral angles, and recent experiments by Maruyama, Rao, and co-workers support this theoretical predication in the metal-catalyzed CVD nanotube growth process.¹⁶⁰ Therefore, it is clear that both thermodynamic and kinetic aspects should be considered for controlling the chirality of SWNTs. For example, chirality-dependent growth rate phenomena of SWNTs can be potentially utilized to fulfill the chirality control based on length selection. That is, SWNTs with the same length have a higher possibility of possessing the same chirality, as compared with nanotubes with distinct different lengths. This may simultaneously fulfill chirality and length sorting of SWNTs in a single step.

3 Electrical transport properties of aligned nanotubes

3.1 Individual nanotube FET

Achievements in nanotube synthesis provide important material platforms to study the properties of nanotubes, especially the electrical transport properties due to their enormous potential in a variety of novel applications such as transparent and flexible transistors, implantable medical devices, and radio-frequency (RF) electronics.¹⁶¹⁻¹⁶⁴ The superior performance and sensitivity of nanotube transistors over silicon transistors can also be used in applications such as chemical, pressure and artificial skin sensors.165-167 As an example, the chemical stability of a SWNT FET was exploited in a salt-water environment, where the electrolyte potential was used to gate the nanotube conduction. As the nanotube transistor was immersed, the gating efficiency was improved and the device showed conceivable single molecule sensitivity even at low voltage.168 Furthermore, nanotube transistors can also act as an alternative to silicon technology beyond the conventional scaling limits for next generation of electronics.169-171

The FETs made from individual SWNTs were first reported more than a decade ago^{172,173} and since then there have been enormous efforts to explore the superior electrical properties of nanotubes such as high current-carrying capacity, ambipolar carrier transport, nearly hysteresis free and high carrier mobility in the diffusive regime.^{174–176} In addition, researchers have also worked extensively to improve the device performance by carefully studying the metal contacts in relation to the nanotube diameters, improve device structures and fabrication techniques, as well as scaling down the channel dimensions.^{170,177–179} Up to date, individual nanotube FETs have demonstrated the measurement intrinsic mobility of 100 000 cm² V⁻¹ s⁻¹ at room temperature, conductance close to the ballistic transport limit ($G = 4e^2/h = 155 \ \mu$ S) with current-carrying capability up to 25 μ A per nanotube, and on/off ratio reaches up to 10⁷ and an on-current density of 2.41 mA μ m⁻¹ which is more than four times the diameter-normalized current density at an operating voltage of 0.5 V with the channel length of sub-10 nm range.^{178,180-182}

The power of transport measurements on individual nanotube transistors has been truly remarkable in elucidating the basic electronic and physical properties of nanotubes. For instance, Kim and co-workers fabricated a series of FETs along a single SWNT with channel lengths ranging from 200 nm to 400 µm to determine the length dependent resistance of nanotubes (Fig. 10a).¹⁸³ Fig. 10 illustrates the conductance of metallic (Fig. 10b) and semiconducting (Fig. 10c) nanotubes at room temperature for selected channel lengths respectively. The mean free path can then be deduced from the linear scaling of the channel resistance. A similar approach can also be used to study the effect of device geometry, substrate, and metal contact on the electrical performance of nanotube transistors.43,170,177 Recently, the IBM group have demonstrated the relationship between channel length and contact length with device performance by fabricating a set of transistors on an individual SWNT with channel lengths ranging from 15 nm to 3 µm, and the SEM image of such device is shown in Fig. 10d. The transfer $(I_D - V_{LBG})$ and output $(I_D - V_{DS})$ characteristics of the device with channel lengths of 15 nm, 300 nm and 3 µm are shown in Fig. 10e and f, respectively. The highest room-temperature conductance (0.7 G) and transconductance (40 µS) were observed with the shortest channel length of 15 nm.

Moreover, it is essential to fabricate devices with single nanotube present in the channel to fully comprehend the transport properties of each nanotube, since the properties of individual nanotubes have been shown to vary strongly from one to another, especially the electrical properties which are very sensitive to their diameter and chirality.^{6,184,185} Zhou et al. measured the electrical performance of individual semiconducting nanotubes of various diameters.186 Fig. 11a and b show the AFM images of two semiconducting nanotubes with diameters of 2.8 nm and 1.3 nm respectively, and their I-V curves measured at 4 K are shown in Fig. 11c and d. They found that at room temperature and zero gate voltage, the resistance of semiconducting SWNTs was typically in the range of 160-500 $k\Omega$ for nanotube diameters larger than 2.0 nm, but the resistance of nanotubes with diameter smaller than 1.5 nm was typically on the order of mega Ohms or higher. Javey et al. also observed ambipolar FET behavior with large diameter (3-5 nm) semiconducting nanotubes,187 in contrast to small diameter ones which typically exhibit unipolar p-type characteristics under ambient conditions due to the charge transfer between nanotubes and adsorbed oxygen molecules. Therefore, it is highly desired to synthesize nanotubes with the same diameter.

With the recent achievement in the chirality controlled growth of SWNTs from the VPE approach,¹⁵³ one can obtain long nanotubes with controlled orientation and chirality, which would eliminate problems of diameter variations mentioned above and help to improve the device-to-device uniformity. Electron transport measurement was carried out with (7, 6) nanotubes after VPE growth. The device schematic and a SEM image of a representative device consisting of an individual (7, 6) nanotube are shown in Fig. 11e and f respectively. The transfer and output characteristics shown in Fig. 11g and h indicate that the device is made of a semiconducting nanotube, as expected from (7, 6) chirality.

3.2 Aligned nanotube array FETs

Despite the fact that promising potential and tremendous achievements have been made in individual nanotube transistors, this remarkable material has not yet found its commercial value in nanoelectronics. This is largely due to the fact that the properties of nanotubes are not only dependent on their chirality



Fig. 10 Individual nanotube FETs. (a) SEM image of a long nanotube contacted with electrodes of various distances. I_{SD} versus V_G of selected channel lengths for (b) metallic tube (M1) and (c) semiconducting tube (SC3) respectively. Adapted from ref. 183 with permission. Copyright 2007 American Physical Society. (d) SEM image of a set of transistors on the same nanotube with different channel lengths. (e) Sub-threshold I_D-V_{LBG} curve from devices with channel lengths of ~15 nm, 300 nm, and 3 μ m. (f) Output I_D-V_{DS} characteristics. Adapted from ref. 170 with permission. Copyright 2010 Nature Publication Group.



Fig. 11 Individual nanotube FETs. (a) AFM image of sample #1 with the nanotube diameter of 2.8 nm. (b) AFM image of sample #2 with the nanotube diameter of 1.3 nm. (c) *I–V* curves of sample #1 under $V_G = 1.5$ V, 0 V, and +1 V at 4 K. Inset: *R vs. T* and the solid line shows the $\exp(-E_a/k_BT)$ fitting of the data. (d) *I–V* curve of sample #2 measured at 4 K ($V_g = 0$). Inset: *R vs. T⁻¹* and the solid line shows the fitting curve. Adapted from ref. 186 with permission. Copyright 2000 American Physical Society. (e) Schematic and (f) a SEM image of a back-gated (7, 6) nanotube transistor with a scale bar of 5 μ m for (f). (g) Transfer characteristics (I_D-V_G) of the transistor measured at various V_D biases. Inset, transfer characteristics plotted in the semi-logarithm scale with $V_D = 1$ V. (h) Output (I_D-V_D) characteristics of the same device measured at various V_G biases from –20 to 20 V. Adapted from ref. 153 with permission. Copyright 2012 Nature Publication Group.

but also on the environment like inadvertent doping from the ambient oxygen can strongly affect the device performance. In addition, interface traps, nanotube defects, and the cleanness of the nanotubes can all have an effect on the performance of each nanotube transistor which will cause large device-to-device variations. Consequently, individual nanotube FETs provide a good platform for the basic study, while they are not practical for applications at this moment.

Nanotube arrays, on the other hand, have abundant SWNTs in the channel areas and thus the influence of nanotube chirality and electronic properties will be averaged to reduce the device-to-device variations dramatically. Another advantage is that the high drive current, which is important for practical applications, can be provided by such transistors since many nanotubes contribute simultaneously to the conductance. CVD growth on crystalline substrates like sapphire and quartz is an effective approach to grow nearly perfectly aligned SWNT arrays and the direct use of such arrays as channel materials has been extensively explored.^{46,54,62,63,188,189} Fig. 12a shows the schematic of a top gate structure FET based on aligned SWNT arrays grown on quartz. The SEM image in Fig. 12b shows the SWNT arrays in the channel area, where perfectly aligned SWNTs with good linearity populated. For such horizontally aligned SWNTs, each SWNT in the channel area may directly connect to the source and drain electrodes if the channel length is shorter than the nanotube length. Therefore, large drive current up to \sim 1 A and a high mobility of >1000 cm^2 V⁻¹ s⁻¹ were reported with a nanotube linear density of ~5 SWNTs per micron (Fig. 12c).189 The drive current can be further improved by improving the SWNT linear density. For example, as discussed earlier, by combining low pressure CVD and multiple stacked transfer, we were about to achieve a nanotube linear density of ${\sim}50$ SWNTs per micron. Fig. 12d shows the relationship between normalized on current and the numbers of transfer, where a clear increase of drive current with increasing transfer times was observed. By further decreasing the channel length down to 0.5 μm, combining with high nanotube linear density, a very high

normalized drive current of ~100 μ A μ m⁻¹ was achieved (Fig. 12e). Such high mobility FETs based on aligned SWNT arrays can find applications in the area of RF and analog circuit applications. In addition, as grown aligned SWNT arrays can be transferred to glass or PET substrates to build transparent and flexible FETs,^{189,190} which renders the device with multifunction and suitable for multipurpose applications.

As mentioned before, as grown SWNTs are typically a mixture of metallic and semiconducting ones, which leads to a very low on/off ratio, *e.g.*, less than 10 for most of the as grown SWNT array FETs. Such electronic heterogeneity prohibits the applications of aligned SWNT array FETs in digital circuits where a high on/off ratio is critical. Over the past five years,



Fig. 12 Aligned nanotube array FETs. (a) Device structure. (b) SEM image of SWNT arrays in the channel area. (c) Dependence of normalized on current (I_{on}/w) and mobility on the channel lengths of the devices.¹⁸⁹ Adapted from ref. 189 with permission. Copyright 2007 Nature Publication Group. (d) Dependence of normalized on current on the channel lengths of the devices from high density SWNT arrays with the device structure shown in the inset. (e) Transfer curves of aligned nanotube array FETs with submicron channel length before (black) and after (red) electrical breakdown to remove metallic SWNTs. The inset of (e) shows a SEM image of the SWNTs in the channel area.⁶³ Adapted from ref. 63 with permission. Copyright 2010 Springer.

several methods have been demonstrated to be able to directly grow semiconducting enriched SWNTs in horizontally aligned SWNT arrays, as we have detailedly discussed in the previous section. By using such semiconducting enriched SWNTs, a simultaneous high mobility and high on/off ratio can be achieved. Shown in Fig. 13a and b are the SEM image and transfer curves of semiconducting enriched SWNTs synthesized from a methanol and ethanol mixed carbon source.115 Around 500 SWNTs were included in the channel while the FETs still possess decent on/off ratios mostly fall into 18-32. A medium on/off ratio of 20 was obtained for SWNT arrays synthesized from isopropanol as carbon source, which is significantly higher than the SWNT arrays grown from ethanol with a medium on/off ratio of 3.5, a value not far away from the expected value of 3 based on un-enriched SWNT arrays (Fig. 13c and d).¹¹⁶ If we consider that metallic and semiconducting SWNTs can carry equal current at their on states, then an on/off ratio of 20 will roughly correspond to a semiconducting SWNT purity of 95%.

Thanks to the achievements of metal/semiconductor separation of SWNTs in recent years, another attractive approach to obtain semiconducting enriched SWNT arrays is to use semiconducting sorted SWNTs and assemble them into horizontal aligned arrays on substrates. Surface self-assembly, spin coating, and gas flow direction methods have been reported to fabricate SWNT arrays with a certain degree of alignment on substrates and were further used for aligned nanotube array FETs.¹⁹⁰⁻¹⁹⁴ As an example, Fig. 13e shows an AFM image of ultrahigh density SWNT arrays, >500 nanotubes per micron, populated on SiO₂/Si substrates.¹⁹³ Fig. 13f shows the effect of channel lengths on the device performance, and a drive current of >120 μ A μ m⁻¹ and a transconductance of >40 μ S μ m⁻¹ were achieved together with a high on/off ratio of $\sim 10^3$. For the solution sorted semiconducting SWNTs, the lengths of nanotubes are typically short, e.g., ~few hundreds of nm to several μ m, which is typically shorter than the channel lengths of the devices. Consequently, most SWNTs cannot connect to both source and drain electrodes. An increase of the SWNT average length was found to be important to improve the carrier mobility.¹⁹⁴

4 Electronic applications of aligned carbon nanotube devices and circuits

4.1 Radio frequency applications of aligned nanotube arrays

Parallel arrays of nanotubes can find various applications in advanced electronics. Among these applications, analog electronics, which only require high transconductance but not high on/off ratio for RF transistors, are of great importance.195-202 CVD synthesis of nanotube arrays is a good solution to achieve scalable assembly of nanotubes and large area horizontally aligned SWNTs can be obtained on certain crystalline substrates.44,46,116,203,204 In this way, this kind of parallel nanotubes provides a great platform for wafer-scale fabrication of RF transistors and circuits. In addition, aligned geometry of asgrown nanotubes allows the gate to control each nanotube without any screening. In contrast, nanotube networks prepared using solution-processed separated nanotubes usually have nanotubes stacked on top of each other, and the gate electric field for some nanotubes can be screened by other nanotubes nearby or on top, therefore leading to weakened gate control. Furthermore, while aligned nanotubes provide direct conduction paths between source and drain, nanotube networks may have tube-to-tube junctions in the channel, which leads to reduced conductance. It is therefore very important to further explore the potential of aligned CVD nanotubes for RF transistors and circuits.

Over the past few years, excellent RF performance based on nanotube arrays prepared by CVD and dielectrophoresis of solution-processed high-purity semiconducting nanotubes has



Fig. 13 Aligned nanotube array FETs based on semiconducting-enriched SWNTs. (a) SEM image and (b) transfer curves of semiconducting SWNTs grown from methanol and ethanol mixed carbon sources. Adapted from ref. 115 with permission. Copyright 2009 American Chemical Society. (c) Device structure and SEM image and (d) transfer curve (red curve) of semiconducting SWNTs grown from IPA carbon sources. The transfer curve (blue curve) of SWNTs grown from ethanol as carbon source was also shown as a comparison. Adapted from ref. 116 with permission. Copyright 2012 American Chemical Society. (e) AFM image of ultrahigh density Langmuir–Schaefer assembled semiconducting-sorted SWNT arrays and (f) effect of channel lengths on the device mobility and on/off ratios from the above assembled SWNT arrays. Adapted from ref. 193 with permission. Copyright 2013 Nature Publication Group.

been achieved in several publications including ours.197,201,202,205 In 2008 and 2009, Kocabas et al. realized RF transistors based on CVD synthesized aligned nanotube arrays with an average density of 5 tubes per µm.197 In this work, an extrinsic currentgain cut-off frequency (f_t) of 5 GHz for a nanotube array transistor with 500 nm channel length (Fig. 14a) was reported. Meanwhile, an intrinsic performance of 30 GHz was estimated after the de-embedding parasitic effects.205 A narrowband amplifier operating in the VHF range based on these aligned nanotube RF transistors was configured with impedance matching and a power gain into a standard 50 Ω load as high as 14 dB was reported at frequency up to 125 MHz.197 Moreover, an amplitude modulation (AM) radio based on these nanotube array transistors, which consists of resonant antennas, fixed RF amplifiers, RF mixers, and audio amplifiers, was demonstrated to receive signals from a local radio station (Fig. 14b). This piece of work is a meaningful milestone for the practical application of nanotube array RF transistors in analog electronics.

Recently, both our group and IBM have achieved intrinsic current-gain cut-off frequency based on nanotube array transistors up to 100 GHz regime.202,206 In IBM's work, dielectrophoresis-assembled high purity semiconducting nanotube parallel arrays were used, showing the importance of good alignment for RF transistor performance.202 For the integration of large-area aligned nanotube arrays for the scalable fabrication of nanotube-based electronics, our group has recently developed a self-aligned T-shape gate fabrication approach for high-performance RF transistors. With this design, the parasitic effects including fringing gate capacitance, access resistance, and gate charging resistance can be significantly reduced. Furthermore, the channel length was scaled down to 100 nm and gate dielectric was reduced to 2-3 nm Al₂O₃, which led to the quasi-ballistic and quasi-quantum capacitance operation for nanotubes.²⁰¹ The self-aligned T-gate RF transistor design was successfully applied to CVD-synthesized aligned nanotube

arrays, combining the advantages of having aligned nanotubes and the reduced parasitic provided by the self-aligned T-gate approach (Fig. 14c). An extrinsic current-gain cut-off frequency up to 25 GHz before any de-embedding procedure was achieved for T-gate aligned nanotube transistors, and after de-embedding, the intrinsic cut-off frequency further went up to 100 GHz regime.

Armed with the excellent on-chip performance of selfaligned T-gate nanotube transistors, our group further analyzed the linearity properties and carried out an extensive analog circuit study including mixing (Fig. 14d) and frequency doubling circuits (Fig. 14e), as the first time that demonstrated the self-aligned nanotube transistor-based analog circuits operated in the gigahertz regime. These results reveal that nanotubes are very promising building blocks in the future high-frequency electronics field.

Further improvement is still required to advance nanotubebased analog electronics. On-chip performance of the nanotube RF transistor is still limited by factors such as contact resistance and current saturation. Controlled synthesis of high density, large-diameter and high-purity semiconducting nanotube arrays is expected to further optimize the nanotube-based RF transistors. Furthermore, the nanotube is predicted to offer inherent linearity compared with other bulk materials. Nanotube RF transistors are anticipated to enable the emerging analog and RF/microwave circuit and system designs requiring highly linear transistors.

4.2 Digital electronics

CNTs are also good candidates for the digital electronics than traditional silicon due to their high carrier mobility and current-carrying capacity. Since 2000, nanotubes have also attracted tremendous attention in the digital electronics application.²⁰⁷⁻²¹⁰



Fig. 14 Nanotube RF devices. (a) SEM of nanotube array transistors. (b) Image of a radio that uses carbon nanotube array transistors for all of the active components, with zoom in views of SWNT transistors wire bonded into DIP packages.¹⁹⁷ Adapted from ref. 197 with permission. Copyright 2008 *Proc. Natl. Acad. Sci. U. S. A.* (c) Schematic of a self-aligned T-gate aligned nanotube array transistor. (d) Output spectrum of a nanotube array transistor-based mixer. (e) Output spectrum of a nanotube array transistor-based frequency doubler.²⁰⁶ Adapted from ref. 206 with permission. Copyright 2013 American Chemical Society.

On the basis of individual nanotube transistors with good switching characteristics, people started studying the possibility of building digital circuits such as logic gates based on these single nanotube transistors. In 2001, by applying both methods of potassium doping and vacuum annealing, Avouris *et al.* realized n-type CNT FETs and firstly built logic gate based on nanotube transistors.²⁰⁸ In this work, a "NOT" gate or voltage inverter with integrated n-type and p-type nanotube transistors were configured as shown in Fig. 15a. Here potassium doping was used and generated n-type transfer property in nanotube transistors. Fig. 15b demonstrates that this circuit successfully realizes the inverter function, as a first step toward digital circuit application for complicated computing systems.

Aligned nanotubes, with potentially significant advantages in terms of manipulation and integration of nanotubes for device applications, have been grown with the CVD method on either sapphire or quartz substrates from several research groups. Previously, our group reported a high-yield and registration-free nanotube-on-insulator approach to fabricate

nanotube transistors based on massively aligned nanotube arrays synthesized on the sapphire substrate, similar to the silicon-on-insulator process adopted by the semiconductor industry. In 2009, in order to overcome the challenges of small sample size, micrometer-scale channel length, and a lack of controlled doping, our group demonstrated integrated nanotube circuits and wafer-scale fabrication.211 Our processing started with the wafer-scale synthesis and transfer of aligned nanotube arrays on substrates up to 4 inch size. Aligned nanotube array transistors with top-gate were used (Fig. 15c). Based on the sub-micrometer-scale device platform, controlled electrical-breakdown was used to remove metallic and highleakage semiconducting nanotubes to improve the on/off ratio. Meanwhile, potassium and electrostatic doping were applied to convert p-type nanotube transistors to n-type. In this way, a truly integrated CMOS logic inverter based on nanotube array transistors was successfully realized. In addition, a defect-tolerant circuit design was proposed and employed for NAND and NOR gates, as an essential feature for integrated nanotube circuits.



Fig. 15 Nanotube digital electronics. (a) AFM image showing the design of an intramolecular logic gate. A single nanotube bundle is bridged over electrodes to produce two p-type nanotube transistors in series. The device is covered by PMMA and a window is opened to expose part of the nanotube. Potassium is then evaporated through this window to produce an n-type nanotube transistor.²⁰⁸ (b) Transfer characteristics of the resulting nanotube-based intramolecular voltage inverter. Open red circles are raw data for five different measurements on the same device ($V = \pm 2$ V). The blue line is the average of these five measurements. The thin straight line corresponds to an output/input gain of one.²⁰⁸ Adapted from ref. 208 with permission. Copyright 2001 American Chemical Society. (c) Schematic diagram of a back-gated transistor; (2) top-gated transistor; (3) CMOS inverter; (4) NOR logic gate; (5) NAND logic gate.²¹¹ Adapted from ref. 211 with permission. Copyright 2009 American Chemical Society.

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Recently, the group in Stanford has also developed a very large scale integration (VLSI)-compatible metallic nanotubes removal technique, so-called VLSI-compatible metallic CNT removal (VMR) technology.²¹² This technology combines design and processing to create CNT transistors and circuits immune to metallic and mispositioned nanotubes to overcome the challenges of existing techniques. Combinational and sequential CNFET logic circuits such as half-adder sum generators and D-latches have been realized and form the fundamental building blocks of VLSI digital systems. With further optimization in material preparation and circuit design, CNTs are promising building blocks in large-scale low-power digital electronics.

5 Conclusions and outlooks

In this article, we reviewed our understandings on the principles and recent developed methods to control the alignment, diameter, electronic property, and chirality of nanotubes. Moreover, electrical transport properties as well as device and circuit applications of individual SWNTs and aligned arrays of SWNTs have been presented. Ideally, for the applications of nanotubes in electronics, densely packed and perfectly aligned SWNTs with identical and adjustable chiralities are the perfect choice. Despite the fact that much very encouraging progress have been made in the past few years on the controlled synthesis of nanotubes, it is still far away from the above goal, especially for chirality control. Perhaps for the electronic applications of SWNTs, the most urgent and practical task at this moment is to control the electronic properties of nanotubes. Nanotube post-growth separation has been able to enrich semiconducting SWNTs with purity higher than 99%, however, this cannot be achieved in direct nanotube synthesis processes at this moment. With the help of advanced experimental tools and theoretical simulations, our understanding of the nanotube nucleation mechanisms and growth kinetics will be deepened and this would benefit their controlled growth.

On the other hand, fast and accurate characterization methods which are able to examine the metallic/semiconducting and chirality information of as grown substrate nanotubes are highly desired.²¹³ With such techniques available, a prompt feedback to the synthesis community will definitely be very helpful to improve the synthesis recipes and accelerate the controlled synthesis of SWNTs. As the performance of nanotube devices is highly related to their structures and properties, such success in material synthesis will play a dominant role in practical applications of nanotube devices and circuits.

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