CHAPTER 4

ORDERED ARRAYS OF CARBON NANOTUBES

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BACKGROUND

Carbon nanotubes are well known for their unique physical properties, which depend sensitively on the dimensions of the nanotube. It is imperative to develop methods for positioning, orienting, and controlling the chirality and length of CNTs before they can be used in a broad range of applications. One approach, which involves the chemical vapor deposition of hydrocarbons in the presence of catalytic nanoparticles, has worked well and forms the basis for advances discussed in this chapter. Importantly, the CVD approach is amenable for scaled-up manufacturing of CNTs, and it is fully compliant with existing semiconductor processes for the development of CNT-based devices.

This chapter focuses on the synthesis of ordered MWCNTs and SWNTs. A few promising applications that are expected to impact emerging technologies are also discussed. The discovery of the electric-arc (Journet et al. 1997) and pulsed laser vaporization (Thess et al. 1996) methods for bulk production of CNTs has facilitated an in-depth understanding of the fundamental properties of CNTs and numerous applications that exploit the unique properties of CNTs (Dresselhaus, Dresselhaus, and Avouris 2001). However, several drawbacks exist with these bulk growth methods, such as the presence of amorphous nanosized carbonaceous materials, CNTs with a wide range of chiralities (how the graphene sheet rolls up into a tubular form), and randomly oriented bundles or ropes in the sample.

The growth of CNT arrays using a chemical vapor deposition of hydrocarbon precursors in the presence of nanosized transition metal catalysts has helped resolve some of these drawbacks. Arrays of high-quality MWCNTs were prepared from a catalytic decomposition of hydrocarbons on SiO_2-coated silicon and quartz substrates at temperatures that are relatively low (~700°C) compared to those used in the electric-arc or the pulsed laser vaporization methods (Figure 4.1) (Fan et al. 1999; Ren et al. 1998).

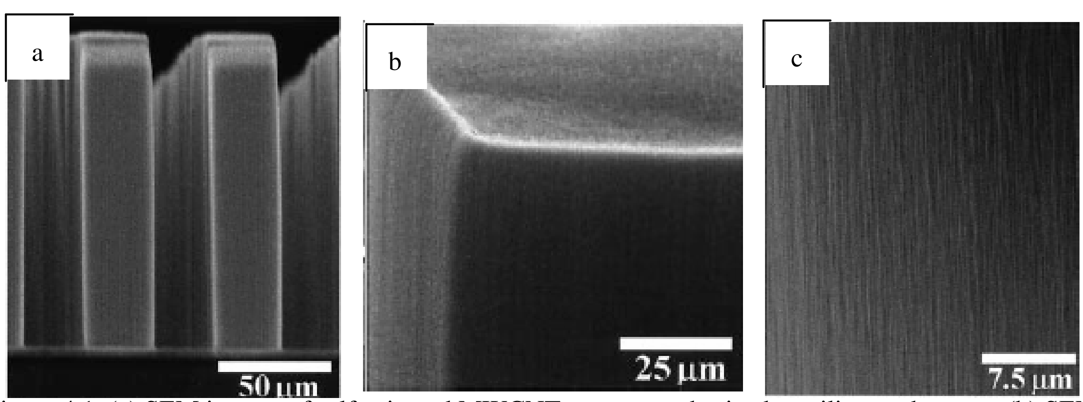


Figure 4.1. (a) SEM images of self-oriented MWCNT towers synthesized on silicon substrates; (b) SEM images showing sharp edges and corners at the top of a nanotube tower; (c) well-aligned MWCNTs in the direction perpendicular to the substrate surface (Adapted from Ren et al. 1998).

CNTs possess remarkable physical properties, however because of their size, they are difficult to manipulate or orient into ordered macroscopic structures for investigating their inherent anisotropic fundamental properties. Due the oriented nature of MWCNTs present in the CVD grown samples, initial studies focused on uncovering the anisotropic optical (Rao et al. 2000) and electrical transport properties (Wang et al. 2001) of MWCNTs. Subsequently, MWCNT arrays grown on large-scale surfaces served as scaled-up functional devices for use as scanning probes and sensors (Service 1998) and as field emitters (Saito et al. 1998). These advances motivated improved growth methods for CNT arrays and the plasma-enhanced CVD method (Ren et al. 1998), and enabled nanotube growth at lower (~450–500°C) growth temperatures with a high degree of control in the placement of CNT arrays on the substrate, and the overall dimensions of the array (Figure 4.2).

(a) (b)

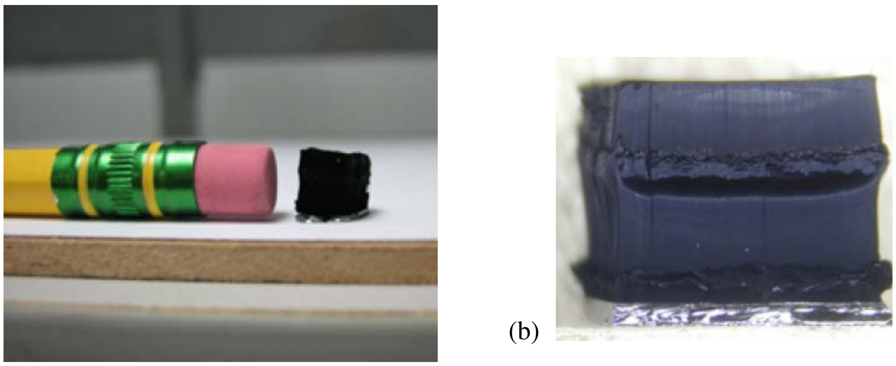


Figure 4.2. (a) Vesselin Shanov and coworkers at University of Cincinnati's Smart Materials Nanotechnology Laboratory used plasma-enhanced CVD to grow 7 mm tall MWCNT arrays on Si substrates; (b) an expanded view of the as-grown MWCNT array image (Ren et al. 1998).

While most of the university-based research has focused on the small-scale growth, characterization, and applications of MWCNT arrays, the Japanese industrial giant Fujitsu focused on the synthesis of large-area, oriented MWCNT arrays on Si substrates since it envisioned the likelihood of achieving dramatic improvements in interconnect technology based on oriented CNTs (Figure 4.3). As the size of electronic devices continues to shrink, the electronic industry is faced with several challenging problems that warrant a concerted R&D effort. For example, there is a growing demand for interconnects that can tolerate high current densities and simultaneously be impervious to electromigration.

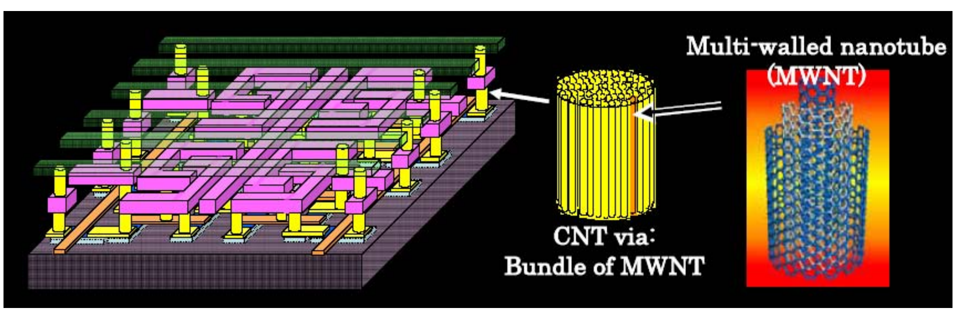


Figure 4.3. A schematic of Fujitsu's vision for integrating vertically aligned MWCNTs as vias for large-scale integrated circuits.

Copper interconnects have proved beneficial, as compared to Al interconnects; a current density of 10^6 A/cm^2 has been achieved. MWCNTs are being explored to push these limits even further; they could serve as very narrow interconnects with a current density approaching 10^9 A/cm^2. In addition to serving as heat sinks, the strong covalent bonds in the MWCNT minimize electromigration, thus providing a solid proof-of-concept for futuristic interconnects. Horizontal interconnects join field effect transistors together in different parts of an integrated circuit. Several layers of horizontal interconnects may be present, and each layer is separated by an inter-level dielectric. The overall assembly is thermally unstable above ~500°C. Vertical interconnects, called vias, pass through holes in the dielectric to join horizontal interconnects to the source, drain, or gate electrodes of an FET.

In December 2005, the Fujitsu team announced that it had developed the world's first CNT-based heat sink for semiconductor chips (Figure 4.4). These heat sinks dissipated large amounts of heat generated by high-frequency, high-power amplifiers; the nanotubes formed the bumps in a "flip-chip" structure. Fujitsu hopes to commercialize this heat sink technology within two years and to deploy it in base stations for next-generation mobile communications in about three years. The Fujitsu team has also developed CNT vias for large-scale integrated circuit (LSI) interconnects for 32 nm chips and beyond. Fujitsu hopes to commercialize its CNT-based interconnect technologies by 2012 (Figure 4.5).

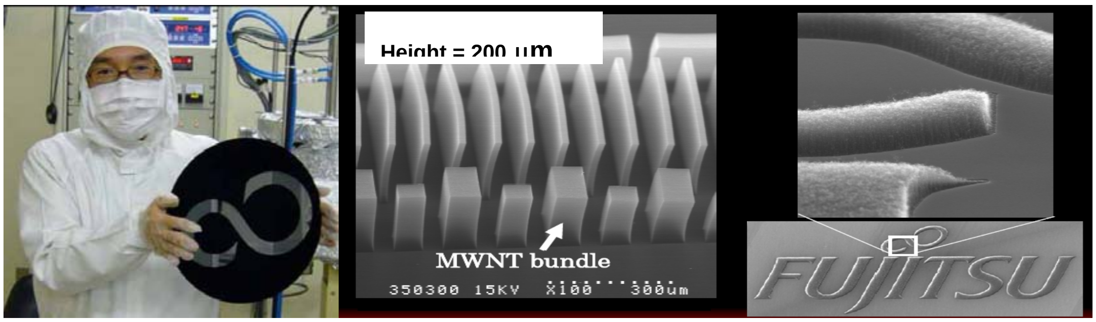
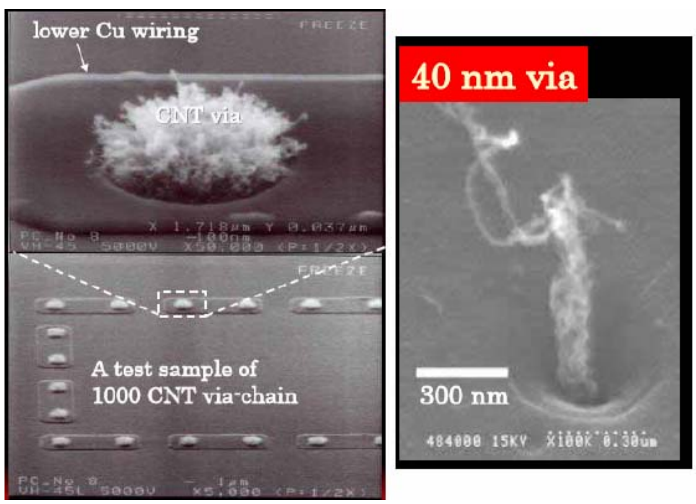


Figure 4.4. Large-area oriented MWCNTs prepared using Fujitu's low-temperature growth process involving hot filament/dc plasma CVD method and Ni and Co catalysts; controlled growth of MWCNT arrays is exemplified on the right.



a b

Figure 4.5. Interconnects for LSI are one of the target applications in Fujitsu's nano technology program. SEM images of a CNT via – chain fabricated at Fujitsu; (a) the via diameter can be tuned between ~1 µm to (b) ~40 nm.

Research in the CVD growth of CNTs is witnessing several rapid developments. Dr. Hata's group at Japan's National Institute of Advanced Industrial Science and Technology (AIST) laboratory has recently reported a water-assisted thermal CVD method for preparing high quality SWNT arrays (Hata et al. 2004).

The group members refer to their process as the "super growth method." It appears to result in a very efficient growth of vertically aligned single-walled nanotube forests (Figure 4.6), with heights up to 2.5 mm and carbon purity exceeding 99%. The super growth method is projected to address many critical problems such as scalability, purity, cost, and realistic applications involving CNTs. It is not clear yet that their tubes have a high degree of order in the tube wall.

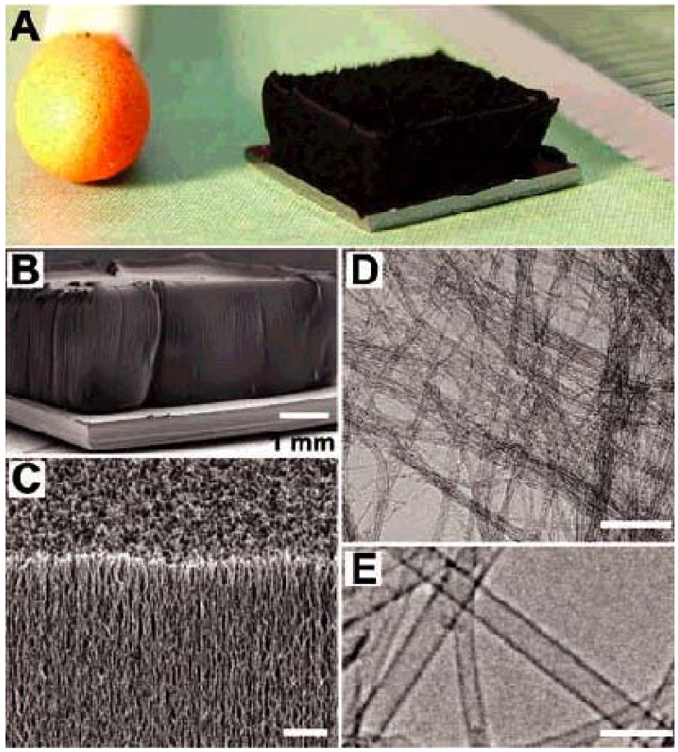


Figure 4.6. Oriented arrays of SWCNTs prepared using the super growth method. The height of the array is comparable to the size of match-stick head shown in panel (a). Subsequent panels show expanded views of the SWCNTs present in the array. The scale bars in panels (b) through (e) correspond respectively to 1 μm, 100 nm, and 5 nm (Hata et al. 2004).

One of the biggest challenges is controlling the physical dimensions of CNTs, as their electrical properties vary depending on length, diameter, and chirality. Controlling chirality is by far the most daunting task, and is viewed as the "Holy Grail" of CNT production. To date, bulk production of mono-chiral isolated SWCNTs has eluded researchers. Recently, Resasco's group at the University of Oklahoma successfully prepared SWNT bundles that predominantly contained chiral SWCNTs (Rao 2000, Ren 1998, Wang 2001, Tan and Resasco 2005). Bimetallic Co/Mo catalyst particles served as the catalyst and reproducibly favored the growth of SWCNTs with chiralities (Rao et al. 2000; Ren et al. 1998; Wang et al. 2001). SWCNTs produced by the electric-arc, pulsed laser vaporization (PLV) or the high-pressured CO conversion (HiPCo) methods do not exhibit any selectivity for specific tube chirality.

A leading fiber and textile manufacturer, Toray Industries, Inc., in Japan, has moved closer to realizing the Holy Grail of CNT production. Toray has developed a low-cost method for producing SWCNT and double-walled carbon nanotubes. Its method is based on thermal decomposition of hydrocarbons in the presence of iron catalyst particles in a temperature range 600–900°C. The dimensions of the catalyst particles are determined by the size of the pores present in the zeolites catalyst support (Figure 4.7). The tight catalyst particle diameter distribution presumably leads to a highly selective tube diameter and chirality distribution. Because of the well-defined size of the catalyst particles, Toray's method is conducive to producing high-quality isolated SWCNTs with well-defined chirality. Presently, the company produces and sells SWCNTs and DWCNTs in bulk quantities.

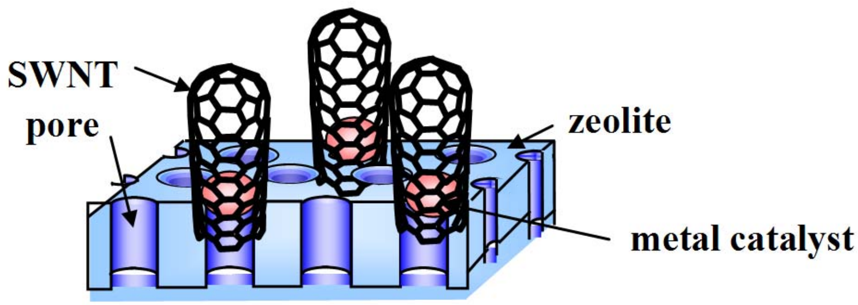


Figure 4.7. A schematic of the template-assisted CVD process developed by Toray Industries, Japan.

Much effort has also been expended in developing CVD methods for growing horizontally oriented MWCNTs on Si substrates (Wei et al. 2003). The results show that vertical and horizontal CNTs can be obtained by manipulating the electric field applied on the substrate and the flow direction of the gases. Recently, Liu and coworkers reported a "fast heating" CVD method that promotes the growth of long and aligned SWCNTs (Huang et al. 2004). They discovered that the rate at which the substrate temperature is ramped during the initial stages of the CVD process leads to the horizontally aligned SWNT arrays depicted in Figure 4.8. Figure 4.8a displays oriented and long SWNT arrays obtained by the "fast-heating" growth process (Huang et al. 2004); the Fe/Mo catalyst nanoparticles are deposited using photolithography, or by a simple deposition process. A mixture of CO/H_2 feed was decomposed at 900°C for 10 minutes to yield the SWNT arrays shown in the image. The right-pointing arrow at the top right corner indicates the direction of gas flow during the nanotube growth. Inset shows a portion of the sample on an expanded scale. Figure 4.8b shows a SEM image of SWNT array that cross over the etched trenches in the Si substrates.

A mechanism dubbed as the "kite-mechanism" has been attributed for the horizontal growth of SWCNTs. Compared with conventional CVD methods, the feed gas, catalysts, and many other experimental parameters in the "fast-heating" CVD are similar. The only major difference between these two methods is the heating rate of the substrate at the initial stage of the growth process (Huang et al. 2004).

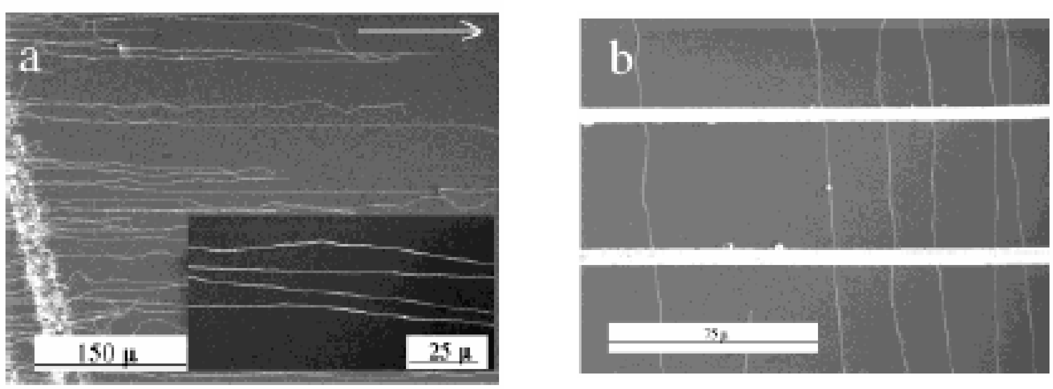


Figure 4.8. SEM images of individual SWCNTs prepared on an oxidized Si surface.

SUMMARY

The CVD method for nanotube growth is paving the way toward selective growth of particular chirality CNTs. Significant advances in the manufacturing of carbon nanotubes with controlled dimensions, and their placement at desired locations with desired orientations, have been achieved. Presently, we are witnessing these advances fuel on a global basis a clear transition in nanotube manufacturing from university bench-top growth chambers to industrial-scale pilot-plants. Very soon, we may overcome the barriers predicted by the legendary Moore's law without upsetting Rock's law (which is viewed as the economic flipside to Moore's Law), if present and future technologies stay focused on ushering in a new era of electronics by integrating CNTs with silicon technology.

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discussed. With small dimensions and a combination of excellent mechanical and electrical properties, nanotubes could find their way into nanoelectromechanical systems. Regarding filler applications, in addition to the epoxy and thermoplastics that are commonly considered, elastomers filled with nanotubes have also been studied. In particular, where mechanical improvements and thermal stability can be achieved by incorporation of nanotubes in elastomers, there will be scope for applications. The use of nanotubes as tiny probes was already mentioned. An extension of this would be applications in bioengineering. Nanotube tips functionalized with biomolecules can be used in imaging, as well as in manipulation of a variety of biological species. There has even been report of using a pair of nanotube tips to function as tweezers for nano-manipulation. Polymer composites stiffened with nanotubes could provide the next generation of stents in biomedical implant applications. Microcatheters made from polymer (Nylon-12) nanotube composites have already been demonstrated (Endo et al. 2005); these provide better handling and blood-coagulation properties and higher stiffness compared to pure polymer. Organized nanotube structures can also provide new and fascinating avenues of applications. Arrays of nanotubes grown on microscale fibers can act as brushes (nanotube bristles) which can be useful in a variety of applications ranging from cleaning micro-trenches to contact brush-switches.

CHALLENGES AND FUTURE PROSPECTS

The mechanical applications of nanotubes will probably require the largest volume of nanotubes. Among these, fillers in polymer composites and mechanical stabilizers in batteries dominate the scene. The biggest challenge will be to figure out the right way to disperse the nanotubes in composite structures. It does not look promising for nanotubes to replace existing carbon fibers in structural applications where the fibers are the load carrying elements. Unless nanotube-based long fibers can be spun in a scalable manner, and these fibers challenge the mechanical properties of traditional carbon fibers, this will be a tough task. However, novel ways of incorporating nanotubes into the existing framework of composites would ensure large volume demand for nanotubes. Incorporation of nanotubes to improve through thickness properties of 3D composites, or introduction of dispersed nanotubes in polymer matrices to improve vibrational damping, are examples of this scenario. Nanotubes as matrix modifiers and solid state curing agents could allow the large-scale entry of nanotubes into polymer composite structural applications. In order to obtain high-strength polymer composites with nanotube fillers alone, we would need complex interfacial engineering, and it is not clear if this would be cost-effective or if this would provide significant enhancements in properties that would justify its use. For the time being, the largest bulk application seems to be the mechanical stabilizing effect of MWCNT in battery electrodes due to the excellent mechanical resiliency of these nanotubes.

Other major challenges in the mechanical applications of nanotubes concern bulk manufacturing and processing of the different types of nanotubes that are available. To date, MWCNTs seem to be winning the battle, particularly due to the fact that these are available today in large quantities, and also, certain properties of these structures (such as resiliency) have been found valuable for specific applications. SWNTs seem to be a more difficult material to work with from the perspective of manufacturability, processing (exfoliation of bundles), and interfacial properties. However, it needs to be remembered that SWNTs are a new material (compared to MWCNTs, which have been under development for over two decades) and clearly possess better properties compared to MWCNT. One could imagine that, ultimately, SWNTs would also find a role in the mechanical applications and become a strong player in the largest-volume application, which is the development of advanced composites based on polymers and nanotubes.

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