NANOTUBE ENGINEERING AND SCIENCE:
SYNTHESIS AND PROPERTIES OF HIGHLY
ORDERED CARBON NANOTUBE ARRAYS AND
Y-JUNCTION CARBON NANOTUBES

by

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A thesis submitted in conformity with the requirements
for the degree of Master of Applied Science
Graduate Department of Electrical and Computer Engineering
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Highly ordered carbon nanotube arrays and Y-junction carbon nanotubes were synthesized and studied for the first time. These new nanostructures demonstrate the next step towards engineering carbon nanotubes into functional materials for nanoscale science and technology. Highly ordered arrays were fabricated by chemical vapour deposition involving the decomposition of acetylene within hexagonally-disposed nanochannel alumina templates. The nanotube arrays are characterized by a narrow size distribution, large scale periodicity and high densities. Y-junction tubes were grown similarly in high density arrays, using Y-branched template channels. These novel nanotube junctions consist of a large diameter tube branching into two smaller diameter ones. Electronic transport measurements on Y-junction nanotubes showed them to possess intrinsic and reproducible rectifying behaviour at room temperature. The results could be explained by considering the change in bandgap across the junction caused by joining together different diameter nanotubes and illustrate a new type of semiconductor heterojunction for nanoelectronics.
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**Fig. 5.4.** Infrared detector based on Y-junction nanotube array. The incoming light is brought to the junction region via the wide bandgap branches.
A civilization's development is often marked by the materials it employs; Thus, the stone, bronze or iron age of a culture refers to the progressive mastery of materials by a given people [1.1]. The types of materials used by a civilization and the technologies they enable play an important role in almost every aspect of a culture's way of life, from the individual to society as a whole. Combined with human thought and ingenuity, knowledge about materials has brought about new possibilities throughout history with key innovations such as stone tools, brick, the steam engine, the light bulb, modern computers and telecommunications systems, to name only a few.

1.1 Background and Motivation for Thesis

It may seem that with all the tremendous technological advances of the past century in particular, there is little left to explore in terms of new materials for completely novel technologies. Indeed, materials such as steel and silicon have been refined to unprecedented levels [1.2,1.3]. However, a new field is now emerging in which materials are controlled at the nanometre scale, making the possibility of creating new things appear almost limitless [1.4].
1.1.1 Nanomaterials and Technology

The emerging fields of nanoscience and nanoengineering refer to the study and application of materials that range in size from approximately one nanometre (nm) to several hundred nanometres. The ability to manipulate matter at this intermediate scale between individual atoms and several thousand molecules is attracting the attention of scientists and engineers for several reasons: As materials are pushed down to finer scales qualitatively new phenomena appear allowing novel technologies to be realized; Traditional models and theories for material properties and device operations are based on "critical length scales" that are generally larger than 100 nm [1.5]. Thus, when at least one dimension of a structure is less than this critical length, distinct behavior can emerge which cannot be explained by traditional models and theories. The effects of size confinement, the predominance of interfacial phenomena and quantum mechanics unique to structures at the nanoscale alter the physical, chemical and biological properties of these materials. By designing materials from the "bottom up" atom by atom [1.6], researchers are learning to design new materials with new sets of properties, opening a whole new array of possibilities to explore for materials research. The practical application of these nanomaterials is generally referred to as nanotechnology - a field many believe will impact the way almost everything is designed and made [1.7]. John Armstrong, formerly Chief Scientist of IBM, wrote in 1991, "I believe nanoscience and nanotechnology will be central to the next epoch of the information age, and will be as revolutionary as science and technology at the micron scale have been since the early '70s." More recently, industry leaders have extended this vision: "As we enter the 21st century, nanotechnology will have a major impact on the health, wealth and security of the world's people that will be at least as significant in this century as antibiotics, the integrated circuit and man made polymers. The total societal impact of nanotechnology is expected to be much greater than that of the silicon integrated circuit, for example, because it is applicable in many more fields than just electronics." [1.8].

Evidence is already mounting that nanomaterials will be used widely used in the future:
Synthetically prepared nanostructures typically have very high surface area to volume ratios and, since atoms at surfaces are often reactive, their behaviour is expected to differ from ordinary bulk materials. For example, recent research has shown that gold nanoparticles 3 to 5 nm in size are highly selective in partial oxidation reactions and can catalyze the oxidation of carbon monoxide at temperatures as low as -70 °C [1.9]. Nanostructure catalysis is also currently in use by Mobil Corporation and is the basis for their significant share of the global $210 billion catalyst market. Materials with nanometre dimensions are also being shown to display unique and desirable mechanical properties. For instance, nanocrystalline pure metals with a grain size of about 10 nm have been shown to be two to seven times harder and stronger than those of larger grained (~1 μm) metals [1.8]. Thus, by incorporating nanometre size particles into bulk materials, researchers are hoping to develop materials that will last much longer for applications such as wear-resistant tires, improved coatings for cutting tools, and printing dyes and pigments. Other research is aimed on synthesizing precisely controlled molecules and other nanomaterials and assembling them into bulk materials which are lighter, stronger, programmable and have lower-failure rates. New materials for fuel efficient cars, aircraft, rockets and space stations are all under development.

Solid state devices also stand to benefit greatly by incorporating nanostructures into their designs. For example, within ten years of the discovery of the new phenomenon of giant magnetoresistance (GMR) in alternating nanometre thick layers of magnetic and nonmagnetic metal films [1.10], this nanotechnology has completely replaced older technologies for hard disk magnetic read heads, allowing storage capacity to increase by twenty-fold [1.8]. A future application of GMR is nonvolatile random access memory that will compete in a $100 billion worldwide market. Electronics is another potential breakthrough area for the application of nanomaterials: The Semiconductor Industry Association has developed a roadmap predicting the continued exponential increase in capacity (miniaturization) and performance of CMOS designs. This projection ends in 2012 with structures less than 100 nm - the beginning of the nanoscale regime. No projections have been made past this point for several reasons; current silicon field-effect transistor designs do not appear optimal at the nanometre scale and the effects of
reducing their dimensions to the point where statistically less than a one electron would be available to switch the transistor are generally unknown [1.11]; the integration of such nanodevices into systems is currently an intractable problem [1.12]; even if one could somehow shrink present device designs to the nanoscale while preserving device functionality and attaining phenomenal device integration density, the resultant chip would generate enough heat to melt all its wiring interconnections [1.13], rendering it useless; and finally, estimates predict that the fabrication facilities required to manufacture current silicon technology will cost upwards of $30 to $50 billion in 2010 and the costs are increasing significantly faster than the market is expanding [1.11]. Building structures at the nanometre scale and the new properties they can display is offering several alternatives for future electronics and computational devices that would potentially improve the efficacy of computers by factors of millions, while decreasing size, weight and power consumption to minimal levels. Some of these alternatives include self-assembled molecular electronics using nanometre scale diodes and transistors connected by wires that dissipate little or no heat [1.12], new computational architectures that rely on regular nanostructure arrays that transfer information via local fields rather than global wiring, such as quantum-dot cellular automata [1.13] and quantum switches and logic [1.11]. Other potential uses of nanostructures in the enormous field of solid state devices include patterned nanoscale arrays to store information at extremely high densities and nanometre scale lasers and nanosensors capable of transmitting and receiving data at unprecedented rates, all at low costs and minimal power consumption. It is little wonder then that companies such as IBM, NEC, Motorola and Hewlett-Packard are all actively engaged in nanostructure research.

The nanometre scale is also the natural spatial context for biological systems - "natural nanotechnology" (Fig. 1.1). The possibility of using engineered nanostructures to interact with human cells, in order to treat diseases for example, has spawned a concerted effort, often referred to as nanobiotechnology, poised to revolutionize healthcare and medicine [1.8]. Potential applications include rapid, more efficient genome sequencing for diagnosing and detecting disease effectively and inexpensively; new nanostructured vaccines and routes for drug delivery that target previously inaccessible sites in the body
Fig. 1.1. F1-ATPase complex. This example of a natural molecular machine enables cells to carry out basic functions by aiding in the synthesis of ATP - the fuel for cellular activity. These complexes generate rotary motion like fan motors [1.7].

using designer nanoparticle containers; and new generations of prosthetics and medical implants that are more durable and rejection-resistant.

The above examples are a very small and necessarily limited indication of the possibilities that exist in the rapidly growing field of nanotechnology. By employing devices from different areas, such as using nanostructured optical sensor arrays as implants for artificial eyes, a host of even more potential applications appear, showing the rich interdisciplinary nature of nanotechnology. It should come as no surprise then that a world-wide effort on the part of governments is underway to support the additional research and development needed to bring nanotechnology to fruition. Over $1 billion in federal support will be spent for nanotechnology world-wide in fiscal 2000, led by Europe, Japan and the United States [1.9]. In these countries industry is also supporting nanotechnology at levels comparable to or greater than that of the government. These levels are expected to more than double in 2001 and other nations should soon follow suit, lest they fall behind and be regulated to supporting roles; Whoever becomes most skilled and knowledgeable at the nanoscopic scale will probably find themselves well positioned in the ever more technologically based and globalized economy of the 21st century [1.7].
1.1.2 Tools and Methods of Nanofabrication

"Nanotechnology is the builder's final frontier," remarks Nobel laureate Richard Smalley, Rice University. At the heart of nanoscience and engineering is the ability to build things precisely using nanometre size building blocks. While the pyramids in Egypt, the Golden Gate Bridge, automobiles, microelectronics and man-made polymers all display technological mastery attained over different length scales, the nanometre scale, lying between chemical reaction lengths and microscopic structures, has yet to be mastered. In this sense one can say that nanotechnology is the ultimate form of civil engineering - building structures and machines atom by atom, at the scale where fundamental properties are defined. In order to realize the potential benefits nanotechnology has to offer, new methods to synthesize and manipulate nanoscale objects are needed. Some of the tools being developed for such nanofabrication include scanning probe methods, conventional microelectronics processing and molecular self-assembly.

Scanning probe microscopy (SPM) involves using very fine tips to scan surfaces. The first instance of such a technique was the scanning tunneling microscope (STM) developed by Nobel laureates Binning and Rohrer at IBM in 1981: By scanning a very small radius tip a few atomic diameters above a surface one can detect electrons tunneling across the gap between the surface and the tip. Since the tunneling current varies exponentially with the tip to surface distance this method provides a very sensitive probe for both imaging and manipulating atomic and molecular scale objects and surfaces (Fig. 1.2). The tremendous success of the STM has spawned a whole array of scanning probe methods such as scanning tunneling spectroscopy, scanning force microscopy and near field scanning optical microscopy [1.14]. Using these methods researchers can analyze the physical and chemical properties of individual nanostructures. This capability is very important for characterizing and understanding the behavior of new prototype nanodevices. The ultrafine imaging and positioning capabilities of SPM can also be used to synthesize nanostructures directly via local oxidation [1.15], nanotip lithography [1.16] or nanodeposition [1.17]. While SPM methods have opened many new doors of discovery and are a critical tool for future nanotechnology, using a single
Fig. 1.2. Examples of atomic manipulation and imaging using STM [1.7]. (a) This famous set of images shows how individual xenon atoms were moved on a nickel surface to form a company logo. (b) A ring of 48 iron atoms forms a "quantum corral" confining some of the electrons on the copper surface to a circular barrier. The resulting standing wave pattern shows the electron probability distribution obeying the standard particle in a box problem of quantum mechanics.

tip for imaging and fabricating nanostructures is very tedious due to the slow serial nature of scanning. Thus, SPM developers are now attempting to use many tips in parallel arrangements [1.18].

The very successful microelectronics industry has been based on using photolithographic methods to create electronic circuits with sub micron features. However, to create structures with feature sizes less than 100 nm using lithographic methods requires electron beam lithography (Fig. 1.3). While electron beam lithography for nanofabrication may be useful for initial trial demonstrations, it has several limitations including material damage caused by the electron beam, prohibitive costs and slow electron beam writing. Another well established fabrication tool is molecular beam epitaxy (MBE). MBE and other related thin film deposition methods allow nanometre scale layers to be created atomic layer by atomic layer. Incorporating such confinement in one dimension into devices has already led to the enormous commercial success of GMR hard disk magnetic read heads (Sect. 1.1.1) and to the huge global market for the quantum well lasers used in CD players and fibre optic telecommunications systems.
Fig. 1.3. Example of a nanoscale floating gate memory device employing a polysilicon nanoscale dot fabricated by electron beam lithography [1.19].

The previous paragraph shows a curious dichotomy of well-established processes that have been used to form nanomaterials; On the one hand, conventional lithographic methods seem ill-suited for adaptation to nanofabrication and on the other, MBE seems perfect for creating thin nanoscale layers of different materials with atomic precision and has already proven very successful in making devices with superior properties. If one could have some sort of "MBE-like" ability to control materials in more than one dimension this would provide the ultimate form of controlling matter and placing individual structures precisely at the nanometre scale. In the past decade or so, scientists have been aggressively developing just such a capability through a variety of methods known collectively as molecular self-assembly: The idea here is to be able to manipulate and assemble nanoscale building blocks in predesignated ways in order to find new routes to make everything from nanocircuit elements to new polymers that control light in optical circuits for telecommunications. Many examples already exist showing the potential uses of molecular self-assembly; The nanostructured catalysts used by Mobil Oil Co. are in fact self-assembled zeolite molecules (Fig. 1.4(a)). Another example at Mobil involves 10 nm cylindrical shaped aluminosilicate pores which have been applied
in both catalysis and filtration of fine dispersants in the environment [1.5]. Various self-assembly methods have also been used to create two- and three-dimensional nanotemplates that can then be impregnated with various materials [1.20-1.23]. Another example is the self-assembly of quantum dots on certain substrates during chemical vapour deposition (CVD) or MBE that has attracted interest as a low-cost method of forming nanoscale particles on surfaces [1.24]. These islands can be made as small as 10 nm, in high-densities and uniform sizes but not yet in regular arrays. Other research has focused on using self-assembly to create individual molecular devices [1.12]: For example electrically conductive wires consisting of single molecules have been demonstrated (Fig. 1.4(b)) and molecular-scale versions of diodes, transistors, sensors and memory elements are currently being sought. Progress has also been made towards building molecular logic gates that could function like present-day microelectronic circuits [1.26]. Connecting such molecular-scale devices into ultra high-density electronic networks is a key challenge for molecular electronics to become a reality [1.12].
1.2 Carbon Nanotubes

One of the most promising materials anticipated to impact future nanotechnology are carbon nanotubes (CNTs). These molecular size tubes form when carbon atoms self-assemble (under the right conditions) into nanometre size hollow cylinders (Fig. 1.5). CNTs are attracting great attention in the nanoscience and engineering community due to their unique mechanical and electronic properties [1.27] including super strength combined with low weight, stability, flexibility, good heat conductance, large surface area and a whole host of intriguing electronic properties such as the ability to be either metals or semiconductors and conduct current with little or no heat loss.

This thesis deals with the synthesis and properties of two new types of carbon nanotube structures; Highly ordered CNT arrays [1.28] and Y-junction CNTs [1.29] were fabricated for the first time as part of this work. These nanostructures are novel examples of synthetic or engineered CNTs required for practical applications. The material and structural properties of these nanostructures were analyzed by various means including high-resolution electron microscopy and SPM. In addition, the first electronic transport measurements of individual Y-junction CNTs were performed by using a novel contact formation technique [1.30]. Independent measurements on both individual Y-junction tubes and arrays of many connected in parallel revealed them to possess reproducible rectifying behaviour at room temperature, illustrating a new type of semiconductor heterojunction promising for future nanoelectronics [1.31]. The Y-junction electronic properties were modeled using classic heterostructure physics, which agreed well with the experimental results and provided insight into the Y-junction material parameters.
Fig. 1.5. Carbon nanotube. A network of carbon atoms wrapped into a nanometre size cylinder gives these materials remarkable mechanical and electrical properties [1.27].

1.2.1 Structure of Thesis

The field of CNTs is itself immense and in Chapter 2 the current state of the art in CNT science and technology is introduced. Following Chapter 2, the results of this work that contribute to the state of the art are presented: Chapter 3 begins with a description of the processing steps required to synthesize highly ordered CNT arrays and Y-junction CNTs, followed by a discussion of the fabrication trials and material characterization. In Chapter 4 electronic transport measurements on both straight and Y-junction tubes are presented and analyzed. Finally, Chapter 5 gives a brief summary of the thesis and proposes future work, ending with a short conclusion.
References


Interest in carbon nanotube research began in 1991 when researchers at NEC Laboratories observed tubular features in the electron microscope images of carbon soot produced in an arc discharge [2.1]. Although similar structures had also been observed much earlier [2.2,2.3], at the time they did not receive much attention as interesting new nanostructures. The initial observations at NEC (Fig. 2.1) have generated a very large CNT research effort that now encompasses universities and industrial centres around the world [2.4]. The nanoscale tubular structure of these materials imparts unique and diverse physical properties and provides an avenue for exploring new physical phenomena [2.5]. In just a few years remarkable progress has been made towards developing effective methods to synthesize CNTs and understanding their behaviour through various experiments. The exceptional properties of nanotubes have led to a great number of proposed applications [2.4] and early device demonstrations have shown much promise.

2.1 Theoretical Properties

The ideal structure of a CNT can be considered as a single layer of graphite wrapped into a cylinder. In addition to such single-walled carbon nanotubes (SWNTs), multiple layers of graphite can also be arranged in a coaxial fashion resulting in what are referred to as multi-walled carbon nanotubes (MWNTs), and these were the first type of nanotubes observed experimentally (Fig. 2.1). The way the graphite layer is wrapped into a tube and the width of the sheet used results in different nanotube structures. The chiral vector,
Fig. 2.1. Transmission electron microscope images of carbon nanotubes produced by arc discharge in 1991 [2.1]. The tubes had diameters between 2 to 25 nm and were multi-walled with an interlayer spacing of 0.34 nm. Schematic cross-sections of the tubes are shown below the images.

defined as \( C_h = n a_1 + m a_2 \ (n,m) \), where \( a_1 \) and \( a_2 \) are unit vectors of the two-dimensional hexagonal lattice and \( n, m \) are integers (\( 0 \leq |m| \leq n \), due to symmetry [2.5]), is used to describe the different types of tubes that are possible. Thus, each pair of integers \((n,m)\) represents a possible tube structure (Fig. 2.2(a)). An example of how a layer of graphite is wrapped into a cylinder is shown in Fig. 2.2(b). CNTs are classified as either armchair \((n,n)\), zigzag \((n,0)\) or chiral \((n,m)\), depending on the shape of the cross-sectional ring around the circumference of the nanotube.

The theoretical electronic properties of ideal nanotubes were first reported in 1992 [2.6]. Those calculations showed that the electronic structure of SWNTs depend critically on both their diameter and chirality (wrapping angle). For example, a slight change in the winding of hexagons along the tube can transform it from a metal to a large bandgap semiconductor. To arrive at the origin of this fascinating behaviour the cylindrical structure of the graphite layer that forms the tube should be considered: Around the circumference of the tube the electronic wavefunctions obey periodic boundary
conditions. Therefore, the wave vector associated with the circumferential direction takes on discrete values, while the wave vector along the (infinite) nanotube axis remains continuous. Thus the energy dispersion relations are essentially one-dimensional versions of those for two-dimensional graphite. The remarkable dependence on diameter and wrapping angle is caused by the difference in the nanotube lattice (and hence its electronic properties) when the tube is wrapped in different ways. For example, by changing the chirality and diameter, the nanotube lattice, both along its axis and around the circumference, displays different periodicity and a change in the number of primitive cells in each direction. These changes affect the band structure and alter the nanotube density of states - critical factors in determining whether a material is metallic or semiconducting [1.3]. By considering the nanotube structural symmetries and their relation to the band structure of graphite, it turns out that tubes for which $n - m = 3i$, with
Fig. 2.3. Electronic properties of ideal CNTs. (a) 2-D graphite sheet denoting circled dots as metallic tubes and the rest as semiconducting [2.5]. (b) Theoretical electronic density of states for typical metallic and semiconducting tubes, calculated within a tight-binding model [1.27].

$i$ an integer, are metallic; all others are semiconducting [2.7]. In particular, armchair tubes are always metallic and zigzag tubes are only metallic when \( n \) is a multiple of 3. These results are summarized in Fig. 2.3(a) which indicates that approximately one third of carbon nanotubes are metallic and the rest are semiconducting. Theoretical plots of the electronic density of states for typical metallic and semiconducting tubes are also shown in Fig. 2.3(b) [2.7]. It can be seen that the spectrum contains spikes corresponding to the onset of successive one-dimensional subbands [2.8]. For metallic tubes the subbands are widely separated and only two of them cross the Fermi level. Thus, these tubes are ideal candidates for observing transport in one-dimensional quantum wires [2.9]. Another important result pertaining to all semiconducting tubes, predicts that their energy gap is inversely proportional to the diameter, \( E_g \propto d^{-1} \) [2.10]. This is consistent with the tube structure which approaches that of semi-metallic graphite for large diameters.

In addition to the extraordinary electronic properties mentioned above, carbon nanotubes are also predicted to possess astonishing mechanical properties [2.11]. The sp\(^3\) carbon-carbon bond in the basal plane of graphite is the strongest of all chemical bonds [2.12]. Thus the tensile strength of CNTs should be among the largest possible for any material.
In addition, the tubular structure imparts a larger radius of gyration compared to a solid cylinder, thus making nanotubes exceptionally rigid structures with lower weight. Theoretical simulations have shown that single-walled nanotubes are about an order of magnitude stiffer than an iridium beam of comparable diameter [2.13]. By using larger diameter MWNTs, stiffness and strength should be even greater.

2.2 CNT Synthesis

The three main techniques used to synthesize CNTs are arc discharge between carbon electrodes [2.1], laser vaporization [2.14] and chemical vapour deposition (CVD) [2.15], all of which have shown their relative merits. In each of these methods carbon atoms self-assemble to form nanometre size tubes of carbon.

The original arc discharge experiments of 1991 produced multi-walled tubes that possessed well-defined graphitic layers. This technique involves placing two graphite electrodes in close proximity for arcing to occur under the application of an electric field. Under these conditions, carbon is consumed from the anode via evaporation. This arc-evaporated material then re-condenses on the cathode and the subsequent deposit contains CNTs. In 1993 researchers found that adding transition-metal catalysts into the carbon electrodes produced tubes with only a single shell (Fig. 2.4). This result was important since the simpler and well-defined structure of SWNTs should allow their properties to be more easily explained. However, the yields for producing single-wall tubes using arc discharge were only a few percent.

A key development came in 1995 when researchers at Rice University reported a laser vaporization technique that could produce SWNTs at yields of up to 80% [2.14]. In this method a laser vaporizes a composite metal-graphite target held at 1200 °C in an argon gas flow. A cooled metal target is then used to collect the graphite vapour and the resulting condensed material contains a large proportion of SWNTs. The tubes formed have a narrow diameter distribution and are usually bundled into "ropes" (Fig. 2.5).
Fig. 2.4. Single-walled carbon nanotubes. The tubes were produced by arc-vapourization of graphite and cobalt and have diameters of approximately 1.2 nm [2.16].

CVD methods to grow CNTs involve the decomposition of a hydrocarbon gas over a catalytic substrate. Both multi- [2.15] and single- [2.17] walled tubes have been grown by this technique. CVD is seen as providing a potentially cost-effective solution for the large-scale production of nanotubes and can allow the controlled growth of CNTs at specific sites for potential device applications.

Although most theoretical predictions assume pure and perfectly cylindrical defect-free carbon nanotubes, in practice such pristine nanotube molecules are difficult to observe. Even the most perfect single-walled tubes produced thus far are only defect-free over certain portions of their length (Fig. 2.5(c)). In addition, major challenges in nanotube growth such as controlling the tube diameter and chirality, still remain. However, as discussed in the next section, experiments on synthesized CNTs have shown that they not only display many of the theoretically predicted properties of ideal tubes, but also show new unpredicted effects.
Introduction to Carbon Nanotube Science and Technology

2.3 Experiments with CNTs

The predicted relationship between nanotube diameter and chirality and their electronic properties (Sect. 2.1) was confirmed recently with the aid of STM [2.18,2.19]. Using an STM tip, researchers were able to obtain atomic-scale images of a SWNT and, by fixing the position of the tip and sweeping voltage, its tunneling conductance as well. Since the tunneling conductance is a direct measure of the local density of states of the nanotube, the electronic structure can be correlated with the local chirality of the tube. Some of these results are shown in Fig. 2.6, which verified that SWNTs can be either metallic or semiconducting depending on their diameter and chirality. Similar results have also been obtained for MWNTs [2.20], but there the situation is not as clear due to their typically larger diameter resulting in increased defects, and the unknown effect of multiple shells on the local density of states.
Electronic transport experiments through CNTs are more complex as the entire tube structure comes into play, not just local properties as is the case for STM spectroscopy measurements. A very large number of transport measurements have been performed on both individual and bundles of single- and multi-walled tubes. The key results of these experiments can be summarized as follows: Conductance measurements on individual SWNTs display either metallic [2.21] or semiconducting [2.22] behaviour at room temperature, consistent with theory and previous STM experiments. Very recent SPM measurements [2.23] of the voltage drop across metallic SWNTs show that they are ballistic conductors over micron lengths (Fig. 2.7(b)), consistent with previous transport experiments which indicated they have very long mean free paths [2.24]. Semiconducting SWNTs, on the other hand, have much higher resistances [2.22] and have been found to be much more sensitive to defects with short mean free paths [2.25,2.26]. In addition, field-effect experiments [2.22,2.27] indicate that charge transport in semiconducting SWNTs occurs predominately via holes at room temperature, i.e. they are inherently p-doped. Turning now to MWNTs, transport experiments have shown them to be diffusive conductors at room temperatures (Fig. 2.7(c)), and that they too are p-doped [2.27].
Fig. 2.7. SPM of electronic transport in CNTs [2.23]. (a) Experimental technique used: An AFM tip held at constant voltage is scanned near the nanotube surface during electrical conduction. The electrostatic force between the tip and the nanotube is a direct measure of the voltage difference between them. (b) Voltage drop across a metallic SWNT between two gold electrodes. The signal is almost constant across the length of the tube with the voltage drops occurring at the contacts - i.e. ballistic transport. (c) Voltage drop across a MWNT between two gold electrodes. The bottom image shows the voltage signal as a function of nanotube length. The linear drop indicates diffusive transport.

A plethora of other experiments have shown that CNTs display many additional remarkable properties: Mechanically, nanotubes have shown a record-high elastic modulus and have been shown to be extremely tough - they do not fracture when bent, but buckle reversibly [2.28]. This combination of stiffness and flexibility is truly unique. Other experiments have shown that CNTs can change their shape when exposed to light or static electric fields [2.29,2.30]. In addition, because of their very small tip radius, nanotubes are very efficient field emitters [2.31]. In other experiments CNTs have displayed spin-dependent transport when connected to magnetic electrodes [2.32] similar to the GMR effect (Sect. 1.1.1), and quantum interference via the Aharonov-Bohm effect [2.33].
Fig. 2.8. Examples of nanotube devices. (a) Field emission display fabricated at Samsung [2.37]. The basic pixel design is shown at the bottom. (b) SWNT field-effect transistor. By applying a gate voltage below the nanotube researchers were able to modulate its conductance by 5 orders of magnitude as shown in the experimental plot [2.22.2.27].

2.4 Applications

The exceptional properties of nanotubes, some of which have been mentioned in this chapter, are being actively pursued for numerous applications. Their high strength and lightweight are being used to develop material strengtheners [2.34] and even for bulletproof vests. In addition, their excellent flexibility and stiffness, coupled with their high aspect ratio has generated great interest for use as SPM tips [2.35]. In other research, several firms around the world are developing nanotube field emitter arrays for use in flat panel displays (Fig.2.8(a)) and this may be the first large-scale commercial application of nanotubes. Another area receiving attention is using CNTs as high-density ion storage material for lithium or hydrogen batteries [2.36].
One possible future field of application for CNTs is in molecular electronics (Sect. 1.1.1). Their small size, ability to be either metallic or semiconducting and the low heat dissipation of metallic SWNTs are very desirable for nanoscale electronic devices and their interconnections. Device demonstrations have already shown that field effect transistors using single nanotubes as the conducting channel can be made that operate at room temperature [2.22,2.27] (Fig. 2.8(b)). Although these devices are clearly prototypes and commercial applications are still far off, they are a first step towards molecular scale devices. For true molecular electronics however, it would be desirable to have the entire device *within* a single nanotube structure, for example by creating junctions between semiconducting and metallic tubes. In this case the entire functionality of a diode or transistor could be contained at the scale of a single molecule.
References


3

Processing

Highly Ordered Carbon Nanotube Arrays and Y-junction Carbon Nanotubes

The ability to produce carbon nanotubes with precisely defined size, shape and position is a long sought-after goal for carbon nanotube science and technology [1.27,3.20,3.21]. In particular, if one could somehow engineer CNT structures to tailor their properties for specific device applications, this would be a significant step towards developing nanotube-based devices. In this chapter it is shown that combining CVD with template based methods allows the controllable production of such synthetic CNT structures. As mentioned in Chapter 2, CVD techniques provide a potentially cost-effective approach to fabricating CNTs in high-yields. In addition, CVD has been used as a basic processing tool in conventional electronic devices for decades and this facilitates the incorporation of CVD-grown nanotubes into other devices or systems, such as silicon circuits. By using CVD within nanotemplates two new types of carbon nanotube materials were fabricated as part of this work: highly ordered CNT arrays and Y-junction CNTs.

The basic fabrication process flow used is shown in Fig. 3.1. In brief, a nanotemplate is first formed from an aluminum sheet via self-assembly (I). The template can then undergo optional pre-growth processing (II), which is followed by CVD in the nanotemplate openings (III). The resulting nanostructures formed within the template are then processed for characterization or device applications (IV). The nanotemplate formation process is described in Sect. 3.1. Sects. 3.2 and 3.3 discuss the CVD template growth of highly ordered CNT arrays and Y-junction CNTs, respectively. In Sect. 3.4 the structural characteristics of these nanostructures are presented and analyzed. Finally, Sect. 3.5 summarizes and discusses the fabrication results.
Processing: *Highly Ordered Carbon Nanotube Arrays and Y-Junction Carbon Nanotubes*  |  30

![Image of process flow for forming carbon nanotubes via CVD within a nanotemplate.](image-url)

**Fig. 3.1.** Process flow for forming carbon nanotubes via CVD within a nanotemplate. I, the nanotemplate is formed via self-assembly from the starting material. II, the resulting template is processed prior to CVD (optional). III, CVD growth within the template channels. IV, post-growth processing.

### 3.1 Nanochannel Alumina

#### 3.1.1 Template Formation

Anodic alumina (Al$_2$O$_3$) films are formed when aluminum is made the anode in an electrochemical cell, commonly referred to as anodization [3.1]. Such anodic films have been used in the surface finishing industry for decades [3.2] and have also been widely used as commercial microfiltration membranes [3.3]. Anodic alumina can either be a uniform thin film or possess a two-dimensional porous structure (Fig. 3.2). Porous alumina films are formed when oxide-dissolving electrolytes are used [3.1]. Fig. 3.3 illustrates the basic steps involved in the formation of these porous films: The aluminum anode is placed in an electrochemical cell consisting of counter electrodes and an acid electrolyte (e.g. sulfuric, oxalic or phosphoric acid). Upon application of a positive bias to the aluminum, anodic oxidation begins. In this process oxygen containing ions from the electrolyte (OH and O$^2$) migrate to the aluminum and combine with Al$^{3+}$ ions to form an oxide film. At the same time, the oxide film is also being dissolved by the electrolyte via electric field-enhanced dissolution [3.4]. Due to temperature fluctuations and irregularities in the aluminum surface the electric field is invariably concentrated at certain points and this causes pores to begin nucleating at the surface. These pores then grow perpendicular to the aluminum surface and the resulting structure consists of an array of nanometre scale parallel pores extending throughout the length of the membrane,
Fig. 3.2. Anodic alumina films. (a) Thin, barrier type alumina film. (b) Porous alumina film formed during anodization in oxide dissolving electrolytes. Each pore is separated from the aluminum substrate by a thin oxide barrier layer [3.1].

3.1.2 Using NCA Templates to Create Nanostructures

There has been increasing interest in the use of NCA as templates for nanomaterials synthesis [1.23,3.8]. By using NCA templates researchers have been able to create various nanostructures including metal (magnetic and non-magnetic) nanowires [3.9,3.10], semiconductor nanorods [3.11], metal nanodots [3.12], and anti-dots [3.5]. By virtue of the NCA template all these structures can be made in two-dimensional hexagonal arrays. This property is very desirable for future nanodevices requiring high-density, uniform and well-ordered nanostructure arrays (Sect. 1.1.1).
3.2 Highly Ordered CNT Arrays

The production of uniform carbon nanotubes in large quantities has proven to be a significant challenge. Some groups have been successful in producing aligned carbon nanotubes [3.13, 3.14] but not uniformly and in regular arrays. Given the exceptional and unique properties of CNTs (Chap. 2) it would be very useful to be able to produce arrays of isolated carbon nanotubes with uniform dimensions (and hence well-defined properties), periodically arranged to meet device requirements for nanotechnology. By using a hexagonally ordered NCA template and CVD, large arrays of parallel carbon nanotubes with an unprecedented level of periodicity and uniformity were synthesized.

3.2.1 Fabrication

The fabrication process begins with the anodization of high purity (99.999%) aluminum to form the nanotemplate that will be used for CVD (Figure 3.1, I). In order to form a hexagonally ordered NCA template a two-step anodization method [3.12] was used:

Fig. 3.3. Anodic oxidation of aluminum. The basic electrochemical cell used to anodize aluminum is shown at the left. A close-up view of the aluminum/electrolyte interface during anodization is shown illustrating the basic steps involved in the anodic oxidation of aluminum [3.15].
First, an aluminum sheet was anodized in 0.3 M oxalic acid at 15 °C under a constant cell voltage of 40 V with graphite counter electrodes (Fig. 3.3, left) for at least 20 hours. This initial film consists of disordered channels and was completely removed using a wet etch in a mixture of chromic (1.8 wt%) and phosphoric (6 wt%) acids for several hours. Subsequent examination of the underlying aluminum metal substrate showed that it was textured in a hexagonal close-packed array (Fig. 3.5(a)) due to the self-ordering of the pores during the anodization process [3.15]. The final step to form a hexagonally ordered NCA template was a second anodization of this textured aluminum film under the same conditions as the first anodization, typically for 1 to 2 hours. This resulted in an ordered array of parallel pores throughout the depth of the film, approximately 30 nm in diameter and several microns in length (depending on the second anodization time) (Fig. 3.5(b)).

The next step, prior to CVD growth, is to electrochemically deposit a small amount of cobalt into the bottom of the template channels [3.16] (Fig. 3.1, II). This is considered to aid in CNT formation during CVD [3.17] and also facilitates subsequent electrical contact to the nanotubes (Chap. 4). The pores of the NCA template were widened to approximately 40 nm by dipping in 0.1 M phosphoric acid for 30 minutes in order to make the cobalt deposition easier, although this step is optional. To deposit cobalt, the barrier layer of the NCA film is first thinned by reducing the anodization voltage to 10 - 12 V in 2-3 volt steps at the end of the second anodization, while allowing the current to recover after each voltage drop [3.18]. This results in a very thin barrier layer that is known to assist in the electroplating of NCA films. Finally, an AC voltage of 14 V (rms)
Fig. 3.5. Results of two-step anodization method [3.12] used to create hexagonally ordered NCA template. (a) AFM images of textured aluminum substrate after first anodization. (b) SEM cross-section image of NCA template after second anodization of surface in (a), displaying hexagonal close-packed parallel channels.

at 100 Hz is applied to the NCA template in an electrolyte consisting of 240 g/L CoSO₄·7H₂O, 40g/L HBO₃ and 1g/L ascorbic acid, with graphite counter electrodes for 30 to 60 seconds to fill the bottom of the template channels with a small amount of cobalt [3.16].

The CVD growth of the CNT array was carried out in a tube furnace, shown schematically in Fig. 3.6. The cobalt-loaded NCA sample was placed inside a ceramic tube and first heated at 600 °C for 4-5 h under a carbon monoxide (CO) flow (100 cm³ min⁻¹), to remove any native oxide layer on the cobalt. For the CVD step the CO flow was replaced by a mixture of 10% acetylene (C₂H₂) in nitrogen at a flow rate of 100 cm³ min⁻¹ (Fig. 3.1, III). In a typical experiment, the acetylene flow was maintained for approximately 2 h at 650 °C to grow the tubes within the template via the thermal decomposition of C₂H₂ [3.19]. The samples were then annealed in nitrogen for 15 h at the same temperature. The resulting samples appeared very dark to the naked eye, in contrast to their bright metallic appearance before CVD in the tube furnace. The scanning electron microscope (SEM, Hitachi S-4500) image in Fig. 3.7 shows a trial result of a highly ordered carbon nanotube array that was formed in this way.
Fig. 3.6. Schematic of tube furnace used for CVD growth of carbon nanotubes. The hydrocarbon gas (acetylene) flows over the nanotemplate where it decomposes into carbon.

3.3 Y-Junction CNTs

The synthesis of carbon nanotube heterojunctions i.e., the connection of two or more different nanotubes, is a key step towards carbon nanotube-based molecular electronics (Chap.2) [3.20-3.23]. However, this will be difficult to achieve using conventional carbon nanotube growth methods [3.24] since the straight tube structure cannot be controllably altered along its length. While ideas for post-growth modifications have been advanced, these are hard to implement in practice and prone to defects [3.25]. By modifying the NCA template method used to create highly ordered CNT arrays, individual Y-junction carbon nanotube heterostructures were directly grown by CVD.
Fig. 3.7. SEM image of highly ordered carbon nanotube array displaying excellent uniformity. The array was ion-milled and wet-etched as described in Sect. 3.4.1. The slight splitting of the tube ends that appears here and in other images below is due to the asymmetric electrode configuration used during ion-milling. This splitting was only observed at the tube ends.

3.3.1 Fabrication

The fabrication steps used to create Y-junction CNTs are identical to those described in Sect. 3.2.1 except in one essential detail - the template used consists of parallel Y-branched nanochannels instead of straight ones. This novel template was formed by first anodizing a sheet of high-purity aluminum as described in Sect. 3.2.1. However, this time the voltage was reduced by a factor of $1/\sqrt{2}$ in steps of 2 to 3 volts approximately midway through the second anodization, in a manner similar to that used to reduce the template barrier layer (Sect. 3.2.1). Since the pore cell diameter is proportional to the anodization voltage [3.1] a reduction of voltage by a factor of $1/\sqrt{2}$ results in twice as many pores appearing in order to maintain the original total area of the template, and this is accomplished by a Y-branching of the pores. The SEM image in Fig. 3.8(a) shows a cross-section of a typical Y-branched template produced in this way, consisting of 3 μm long "stems" and 2 μm long "branches" with diameters of 40 nm and 28 nm respectively. All of the branching occurs at the same depth as indicated by the arrow, corresponding to the start of the voltage drop during anodization. Once the Y-branched template is formed
Fig. 3.8. Controlled growth of Y-junction nanotubes. (a) SEM image of Y-branched template. The template consists of parallel Y-branched pores with stems 40 nm in diameter and branches 28 nm in diameter. The arrow shows where Y-branches start to grow (see inset for close-up). (b) Top-view SEM image of carbon nanotubes aligned in the template after processing the surface (Sect. 3.4.1). The nanotube diameter is larger than the original template pore diameter owing to thermal expansion of the template during growth [3.30]. Top inset, close-up view of the stem top in its hexagonal cell. Bottom inset, close-up of the junction region between stem and branch portions, still embedded in the template.

It is deposited with cobalt and subjected to CVD using the same method described in Sect. 3.2.1. The SEM image in Fig. 3.8(b) shows an example of a the resultant Y-junction CNT array formed.

3.4 Structural and Material Characterization of Samples

The structural properties of CVD-grown CNTs have been studied fairly extensively in the past and are well-established [3.26]. In particular, the growth of nanotubes using acetylene gas in the presence of cobalt during CVD has been shown to produce multi-walled nanotubes that contain some defects along their length [3.27]. Therefore we can expect the highly ordered CNT arrays and the Y-junction CNTs synthesized within NCA templates using the methods described in Sects. 3.2 and 3.3 to also possess a multi-walled, graphitic tube structure. The nanotube samples were characterized by electron microscopies and atomic force microscopy (AFM), as described below.
Highly Ordered Carbon Nanotube Arrays and Y-Junction Carbon Nanotubes

3.4.1 Sample Preparation

Before characterizing the samples several post-growth processing steps were performed in order to prepare them for analysis (Fig. 3.1, IV). These methods also proved very useful for subsequent measurements of the nanotube electronic properties (Chap. 4).

Immediately after removing the samples from the furnace, they were examined, as is, using SEM: As shown in Fig. 3.9(a), the surface appeared relatively flat and a few tube-like structures were scattered on the template surface. However, from this image one cannot clearly discern individual tubes within the template pores. Thus, the samples were mechanically cracked to obtain images below the surface: Fig. 3.9(b) shows that an ~100 nm surface layer exists below which each template pore appears to be filled with an individual nanotube. Both straight tube array and Y-junction samples contained this layer. The most likely cause of this top layer is residual carbon deposited on top of the template during CVD [3.26]. In order to allow a proper examination of the CNT array properties this residual layer was removed by ion-milling the surface at 3kV for 15 minutes in a nitrogen atmosphere at ~10^{-2} Torr [3.28]. After the samples were ion-milled, they were wet-etched for 10-45 minutes (Sect. 3.2.1), in order to dissolve some of
Fig. 3.10. Top-view SEM image of highly ordered CNT array showing hexagonal close-packed geometry. The hexagonal cells have sides approximately 57 nm long and the intercell spacing is 98 nm. The apparent increase in the tube wall thickness is an artifact of the ion-milling procedure. Cross-section images were used to obtain accurate measurements of the tube diameters.

the NCA matrix and expose the nanotubes. The final result is a "forest" of nanotubes arranged in a periodic array as displayed in Figs. 3.7 and 3.8(b).

In addition to observing the samples inside their native NCA template, it is also useful to be able to characterize individual nanotubes separated from the array. To accomplish this, nanotube suspensions in alcohol were prepared using the following procedure: First, as-grown samples were wet-etched for at least 24 hours, until the NCA film was completely dissolved and separated from the underlying metal substrate [3.29]. After removing the metal substrate, the nanotube-containing solution was centrifuged at 5000 rpm for 1 hour. The resulting test tube solution contained a black dust-like separation. This solution was then purged of liquid, diluted with isopropanol or ethanol and centrifuged again. After several such steps a clear solution containing a fine black mist of CNTs in alcohol was obtained. This solution could then be diluted further and dispersed on various substrates as required.
Fig. 3.11. CNT array cross-sections. (a) Tube lengths near the array surface displaying uniform alignment and positioning. (b) Nanotube array partially exposed from the NCA template; the cobalt catalyst is at the base of the tubes separated from the aluminum substrate.

3.4.2 Electron Microscopy

The resultant carbon nanotube arrays were characterized extensively using SEM. Top-views of both highly ordered straight CNT arrays and Y-junction arrays were virtually identical, owing to the NCA template properties (Sects. 3.2.1, 3.3.1). The micrograph in Fig. 3.10 shows a typical top-view of the carbon nanotube arrays after ion-milling and wet-etching the surface, as described in Sect. 3.4.1.

The top-view CNT array images shows several important features of the carbon nanotube arrays produced by this technique: First, all of the nanotubes are parallel to each other and perpendicular to the template forming a periodic hexagonal close-packed array. Second, the nanotubes are of uniform length and are open-ended. Third, each pore of the template is filled with one nanotube, which defines the tube diameter. In addition, the tube diameters were found to be very uniform throughout the array, with an average diameter of approximately 47±0.7 nm - more uniform than heretofore reported using other methods of nanotube array synthesis [3.30]. Finally, the array has a very high tube density of approximately $10^{10}$ cm$^{-2}$. 
Fig. 3.12. Energy dispersive x-ray spectrum for CNT array. The dominant aluminum peak is seen along with weaker high energy peaks corresponding to sample impurities. Below 1 keV detector efficiency is low, however, carbon and oxygen peaks still appear corresponding to the CNTs and the oxide matrix, respectively.

To image the nanotubes along their lengths the arrays were cracked to obtain cross-sections. Fig. 3.11(a) shows an oblique view of a highly ordered CNT array, again displaying uniformity with respect to the disposition and dimension of the CNTs. In Fig. 3.8(b) a cross-section of the branching point of the Y-junction tubes embedded in the template is shown. The larger carbon nanotube (stem) is seen gradually evolving into two 35 nm diameter branches, forming a continuous Y-junction with three clearly separated ports. The bottoms of both straight and Y-junction CNTs contained the electrodeposited cobalt particles as displayed in Fig. 3.11(b).

The SEM also allowed an elemental analysis of the samples to be performed via energy dispersive x-ray analysis (EDX). EDX works by collecting the x-ray photons emitted by the excited inner atomic shells of a sample during high-energy electron bombardment [3.32]. An energy dispersive detector whose signal is proportional to the energy of the absorbed x-ray, allows the characteristic energies of atomic elements in the sample to be
Fig. 3.13. TEM images of carbon nanotube bundles. (a) Bundle of straight tubes with uniform lengths of 6 μm corresponding to the dimensions of the NCA template they were grown in. (b) Y-junction nanotube bundle displaying well-defined branching position occurring halfway down the bundle length.

discerned. In Fig. 3.12 a typical elemental spectrum showing x-ray counts for different elements of the CNT array (straight or Y-junction) samples is shown after ion-milling and a short chemical etch (Sect. 3.4.1). As expected a large peak associated with aluminum appears. Peaks below 1 keV cannot be quantitatively compared since the detector efficiency is very low at these energies [3.32]. However, oxygen and carbon peaks are still evident which is consistent with the oxide matrix and the carbon nanotube components of the samples, respectively. Very weak peaks at higher energies are most likely due to the chemical etching used during processing. The EDX spectrum shows that the CNT arrays are relatively clean and only contain a small amount of impurities due to processing.

Further sample characterization was carried out using transmission electron microscopy (TEM) (Hitachi 7000 or JEOL 2021F). To image the tubes using TEM, drops of nanotube dispersions (Sect. 3.4.1) were placed on holey carbon grids. Fig. 3.13(a) shows a TEM image of a CNT bundle which resulted from completely dissolving the NCA matrix. The nanotubes are very straight and have uniform lengths of 6 μm,
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![Image of TEM images of individual nanotubes.](image)

**Fig. 3.14.** TEM images of individual nanotubes. (a) Straight CNT showing cobalt particle at the base. (b) Y-junction CNT with stem ~ 50 nm and branches ~ 35 nm in diameter. The interior of the tube contains some residual carbon material, most likely caused by ion-milling the array surface after CVD growth (Sect. 3.4.1). It was found that this material could be removed by ultra-sonication of the tubes and additional wet-etching (Fig. 3.18).

Corresponding to the thickness of the NCA film in which they were grown. Fig. 3.13(b) shows a similar image of a Y-junction nanotube bundle, once again displaying excellent uniformity of length. The position of the junction is also seen to be extremely uniform, occurring approximately halfway down the length of the bundle. TEM images of individual tubes are shown in Fig. 3.14, displaying the tube walls. High-resolution TEM images of the tube walls (Fig. 3.15(a)) in straight tubes and each arm of Y-junction tubes [3.33], displayed a graphitic multi-walled structure up to a few nm thick similar to that of other CVD-grown tubes [3.27].

Electron diffraction patterns of the nanotubes were also obtained, to reveal additional information about the tube lattice structure. The diffraction patterns give information about the lattice planes of the nanotube [3.24]: The (002) plane corresponds to the horizontal stacking of layers in graphite, while \((hk0)\) planes correspond to other cross-sections through the hexagonal lattice of graphite. In Fig. 3.15(b) electron diffraction patterns are shown for the nanotubes. Both straight and Y-junction tubes displayed similar diffraction patterns. The observed diffraction patterns show two arcs which can...
Fig. 3.15. High resolution TEM image of nanotube wall and electron diffraction patterns. (a) High resolution image showing multi-layer structure of tube wall [3.33]. The parallel planes correspond to graphitic shells coming out of the page. (b) Electron diffraction patterns for the CVD grown CNTs. The electron beam was directed perpendicular to the tube axis. The rings correspond to the lattice planes of graphite indicated [3.24]. The bottom image is a close-up of the central portion of the pattern showing the (002) arcs. The black marker denotes the approximate direction of the nanotube axis. (c) Electron diffraction pattern of amorphous carbon nanowires [3.38], shown for comparison. No clear features other than the main electron beam are visible.

be attributed to the (002) plane of graphite and two outer rings corresponding to the (100) and (110) planes of graphite [3.13]. Ideally the diffraction patterns should consist of distinct points rather than continuous arcs and rings [3.24]. The observations imply that the CVD grown CNTs contain rotational disorder between graphitic shells and defects within the planes, consistent with previous studies of CVD grown nanotubes [3.27]. For comparison, a diffraction pattern of an amorphous carbon nanowire is shown in Fig. 3.15(c). The amorphous carbon displays no clear features in the diffraction pattern. By using the dimensions of the microscope, the interwall distance ($d_{002}$) of the nanotubes was
calculated [3.34] from the diffraction patterns as approximately 3.5 Å, slightly larger than the interplanar separation in graphite ($d_{002} = 3.35$ Å [3.24]). These observations are consistent with the high-resolution TEM images and the total tube wall thickness (Fig. 3.15(a)) suggests the tubes are composed of approximately 14 graphitic layers or shells.

3.4.3 Atomic Force Microscopy

The very fine imaging and manipulation abilities of AFM tips allowed the mechanical properties of the CVD grown nanotubes to be examined. Experiments were performed using an AFM (Digital Instruments 3100) to ascertain the mechanical behaviour of individual nanotubes lying on flat substrates: Individual tubes were first dispersed on silicon wafers covered with a thin film of silicon oxide [3.35]. Once the tubes were located, the AFM tip was slowly lowered towards the surface using the microscope's fine approach while disabling the feedback controls and setting the scan size to zero. After contact was made with the oxide surface, the tip was scanned to bend the nanotubes. This process is shown schematically in Fig. 3.16(a). Figs. 3.16(b)-(d) show the results of one such experiment on two nanotubes that were lying in a cross. As the AFM scans show, the nanotubes could be bent through large angles (Fig. 3.16(c)), until what appeared to be buckling occurred (Figs. 3.16(d)). These experiments show the very flexible nature of the nanotubes and their ability to withstand large amounts of bending before buckling, as has been shown for other multi-walled nanotubes [3.36]. Such mechanical properties are of great utility when individual nanotubes are required to span large gaps between metallic electrodes for electronic transport measurements without breaking (Chap. 4).
Fig. 3.16. AFM manipulation of individual nanotubes. (a) Schematic of the method used to bend nanotubes using an AFM tip [3.36]. The tip first scans over the tube to locate it and is then lowered beside it. To bend the nanotube the tip is scanned across the surface and pushes against the tube. (b) AFM image of two nanotubes lying in a cross. (c) The nanotubes after they were bent at the cross region. The top tube is seen to smoothly bend in the direction of the tip motion which has left a mark in the substrate. The light coloured band at the bottom of the image is an artifact of the scanning process. (d) Image of the bottom nanotube after being bent through a large angle. The tube appears to be kinked, most likely due to a buckling of the tube walls [2.11]. The inset is a close-up view of the buckled tube walls. (The apparent change in nanotube width from image to image is caused by the finite reaction time of the AFM tip as it scans across the tube surface). (all dimensions in μm).

3.5 Summary and Discussion

The highly ordered CNT arrays and Y-junction CNTs fabricated in this work by CVD within NCA templates possess several significant features: Aside from the excellent uniformity in size and disposition, the nanotubes grow naturally perpendicular to a rigid substrate eliminating the need for extensive post-growth nanotube alignment. In addition, this method of nanotube array synthesis is relatively inexpensive and can be scaled up with the template size without adding significant cost. The gentle
Fig. 3.17. SEM image of highly ordered CNT array containing tubes approximately 35 nm in diameter obtained by varying the anodization conditions.

electrochemical methods used and moderate growth temperature make this technique compatible with standard lithographic processes since the aluminum film used to form the NCA template can be deposited and processed on a variety of surfaces including standard silicon wafers [3.37]. The controlled variation of the nanotube size, density and array spacing depends on easily adjustable parameters such as the anodizing voltage, electrolyte composition and temperature [3.1]. Ordered arrays with selectable diameters ranging from approximately 10 nm to several hundred nm and densities of up to $10^{11}$ cm$^{-2}$ can be formed (Fig. 3.17). Furthermore, by using a Y-branched nanochannel for CVD nanotube growth the natural and controllable formation of a very large number of individual but well-aligned three-port Y-junction carbon nanotubes with excellent uniformity and control over the length (up to several tens of µm) and diameter (10-100 nm) of the stem and branches separately, is possible (Fig. 3.18). Tube lengths of 100 µm or more can be obtained by increasing the length of the pores in the NCA template in which the nanotubes are grown, which can be achieved by increasing the time of anodization.

In conclusion, new ways of "engineering" CNT structures were described in this chapter: Highly ordered carbon nanotube arrays were synthesized over large areas by CVD
involving the decomposition acetylene on cobalt within a hexagonally-disposed NCA template. These extremely uniform arrays could be useful in a variety of applications including high-density data storage, field emission displays and infrared imaging detectors (Chap. 5). Looking further, periodically assembled CNT arrays may be useful for new computational architectures which relay on regular arrays (Chap. 1). The other unique result of this work, that controlled, preferential growth of Y-junction carbon nanotubes can occur instead of the straight variety, is intimately connected with the Y-branched NCA template used in this study. Using a Y-branched nanochannel for CVD growth allows the direct synthesis of Y-junction carbon nanotubes containing a large diameter tube branching into smaller diameter ones. These novel nanotube junctions are potentially very useful for molecular electronics (Chaps. 1 and 2). Hence, experiments were performed to determine the nature of electronic transport across the Y-junction, as discussed in the next chapter.
References


A non-specialized ion-milling apparatus was used to clean the template surface. In order to ion-mill the surface an electrode was attached to the residual surface layer. It was found that this surface displayed good conductivity prior to ion-milling, consistent with it being a graphitic carbon layer.

In order to expedite the etching process, samples were cut into small pieces and mechanically bent during etching to separate the nanotubes from the underlying aluminum substrate.

The average nanotube diameter was larger than the original template pore diameter due to ~20% thermal expansion of the template during CVD growth [3.31].


These images were obtained at Hitachi Japan at the request of Junji Haruyama. High-resolution images of the Y-junction branching region could not be obtained due to electron beam-specimen interactions. This problem is still under investigation.

These calculations were performed by Jing Li.

The wafers were prepared by Hope Chik.


As the trend towards ever smaller electronic devices continues, the search for alternatives to current silicon technology has heightened [4.1]. The tremendous success of the microelectronics industry has been based on the miniaturization of a select few basic device elements, all of which are based on different types of junctions: whether it be the p-n junction in diodes, the heterojunction in transistors, or the metal-oxide-semiconductor junction used in virtually all silicon electronic circuits [4.2]. These junctions possess nonlinear, but monotonic current-voltage ($I-V$) characteristics which allow tasks such as signal processing and computation to be performed. Achieving similar functionality at the nanometer scale is desirable, as it can take maximum advantage of the vast base of existing circuit designs and architectures, and is a primary goal, if not a condition for success, of molecular electronics.

The unique properties of CNTs (Chap. 2) present a good opportunity for the development of molecular electronic devices and previous explorations with CNTs have demonstrated single-electron devices [4.3] and field-effect transistors [2.22,2.27] by placing straight tubes across patterned gate electrodes. Recently, there has been growing interest in a conceptually different approach to forming nanotube devices [3.22,3.23], based on connecting together different tubes to form nanoscale junctions, such as between metallic and semiconducting ones. In this approach, rather than externally modifying or probing the straight tube structure after growth, nanotube junctions are directly formed possessing device functionalities intrinsic to their structure which can be used as building blocks for nanoelectronic devices. However, for this approach to be successful, the controlled production of such synthetic CNT junctions will be required [4.4]. As shown in Chapter
Fig. 4.1. Y-junction CNTs grown by CVD in nanochannel alumina templates. (a) SEM image of Y-junction CNT array in cross-section, as viewed from the larger diameter "stem" side. (b) SEM image of a top-view of the array. (c) TEM image of a Y-junction nanotube removed from the alumina template (Sect. 3.4.1) consisting of a 60 nm diameter stem and 40 nm diameter branches.

3, template-based CVD techniques can allow the reproducible and high-yield fabrication of synthetic CNT structures, i.e. the Y-junction [4.5]. In this chapter, conductance measurements on Y-junction CNTs synthesized using this new method are presented which display intrinsic nonlinear and asymmetric $I$-$V$ behavior at room temperature. The results are then modeled using classic heterostructure transport models for a junction with an abrupt change in band gap due to the change in diameter at the junction. These Y-junctions, in which different diameter nanotubes join in a "Y" structure, represent a new type of nanoscale junction for molecular electronics.

The Y-junction CNTs used for the conductance experiments were fabricated using the procedure outlined in Sect. 3.3. An example of the closely-packed and aligned Y-junction arrays is shown in Fig. 4.1. Electronic transport measurements were performed
Fig. 4.2. Y-junction CNT contacts used for transport measurements on individual tubes. (a) SEM image of an individual 6 μm long Y-junction tube across gold electrodes. (b) High-magnification of tube end near gold electrode showing island-like gold film sputtered prior to application of bias and (c), after application of a bias of 10 V for ~ 90 minutes and limiting current to ~ 1μA. After reaching the saturation current, the bias was gradually decreased and held in a series of steps until the current was observed to be constant at each step. The high local electric field at the tube tip induces the migration of gold particles, forming a low-resistance contact to the electrode.

on both arrayed and individual Y-junctions removed from the templates. The Y-junctions were typically 6 to 10 μm in total length and tubes with stem/branch diameter ratios of approximately 35/28 and 50/35 nm were used for array measurements and 60/40 nm for individual Y-junction experiments. Array densities were approximately $10^{10}$/cm².

4.1 Individual Tube Measurements

For electronic transport measurements on individual Y-junction tubes, they were first removed from their growth template by a chemical etch (Sect. 3.4.1) and then dispersed onto lithographically patterned gold electrodes (Fig. 4.2(a)). The gold electrodes were
Fig. 4.3. Electromigration of gold particles. A voltage bias was applied between two gold electrodes covered with gold nanoclusters. Subsequent examination of the area between the electrodes indicates that the nanoclusters congregated into conducting pathways as shown.

deposited on a Si/SiO₂ substrate and consisted of 50 nm thick, 2 μm wide fingers connected to larger square contact pads [4.6]. To make low resistance contacts to the two ends of the Y-junction a very thin island-like film of gold (or silver) was first sputtered onto the sample (Fig. 4.2(b)). Next, a large bias (typically 10 to 20 V, while limiting current) was applied between the two electrodes containing the Y-junction tube. Initially, no current flow was observed, however, gradually, over a period of 1-3 hours, the current began to increase and eventually saturated to a fixed value. Subsequent examination of the tube ends revealed a migration of gold particles (Fig. 4.2(c)), presumably induced by the high electric field at the tube tips. Similar methods have been used to form Ohmic contacts to C₆₀ films via the field enhanced diffusion of gold [4.7]. Experiments with only island-like films between two electrodes were also performed to verify this effect: After the application of a voltage difference between two gold electrodes the conglomeration of gold particles into wire-like pathways was observed (Fig. 4.3). This method was found to produce reliable contacts to individual Y-junction nanotubes. A typical experimental *I*-*V* plot for an individual Y-junction tube contacted in this way is shown in Fig. 4.4. The *I*-*V* data displays distinct asymmetric and rectifying behavior with current flowing more easily under negative bias.
Fig. 4.4. Experimental \(I-V\) curve for an individual Y-junction nanotube contacted as shown in Fig. 4.2, with 60/40 nm stem/branch diameter ratio. The conductance under negative bias increases rapidly while under positive bias almost zero current was observed. The inset shows the bias configuration that was used. The data was taken with a Keithley 236 source measure unit using a probe station in ambient conditions.

4.2 Array Measurements

Although measurements on individual Y-junction tubes are desirable, the method used in Sect. 4.1 is very time consuming and was only performed for a small number of trial measurements. On the other hand, for an independent confirmation and a statistical distribution of the Y-junction nanotube electronic transport properties a unique opportunity is afforded by measuring the Y-junctions in their arrays as shown schematically in Fig. 4.5(a). The very high density of tubes allowed contact to a large number of Y-junction tubes in parallel to be made. This method provides a large sampling of the Y-junction properties and also permits the uniformity of the Y-junction tubes to be judged. In Fig. 4.5(b) a representative experimental \(I-V\) curve corresponding to \(\sim10^2\) junctions connected in parallel is shown (using the individual tube results as reference). As expected the measured currents are larger compared to the individual Y-junction case and the curve is also smoother due to averaging over many Y-junctions. However, the asymmetry and nonlinearity observed for the individual tubes is still
Fig. 4.5. Y-junction CNT array measurements. (a) Schematic of experimental setup used: Contacts to the Y-junction array were made by first ion-milling and etching the array (Sect. 3.4.1) and then sputtering gold electrodes using a shadow mask on the stem side of the array and using the cobalt catalyst at the base of the array to contact the aluminum substrate [3,31]. Transport measurements were performed in ambient conditions using the same apparatus as for the individual tube experiments. (b) Experimental I-V curve for Y-junction array displaying similar asymmetry and rectification as the individual tube results. The inset shows results obtained for straight tube arrays.

... evident in the array measurements as well. This provides further verification that the observed behavior is intrinsic to the Y-junction structure of the tubes and also shows that the tubes are very uniform. For comparison and to further assess the effect of contact resistance on the data similar measurements were performed on highly ordered arrays of straight CNTs, also synthesized by the CVD template method (Chap. 3). As shown in the inset to Fig. 4.5, the straight tubes display an almost linear I-V characteristic that is highly symmetric, providing more evidence that the nonlinear and asymmetric I-V behavior observed for the Y-junction tubes is an inherent property of the Y-junction.
Fig. 4.6. SEM images of gold contacts used for array measurements. (a) Low-magnification view showing array of contacts sputtered on CNT array surface. Some large cracks are visible, but the contacts appear fairly uniform at this scale. (b) Higher magnification view showing extensive cracks on the gold surface. Inset shows a close-up view of the gold film covering the CNT array.

The number of tubes that were contacted in the array measurements should in principal be defined by the size of the sputtered gold contacts. However, closer examination by SEM revealed that the contact pads contained cracks along their surface and that the gold film was not uniform (Fig. 4.6). Subsequent conductance measurements across the gold pad surfaces revealed they were not shorted, implying that they do not consist of continuous films. Indeed most of the CNT array I-V data taken displayed relatively low currents (Fig. 4.7). Thus, the actual number of tubes measured is clearly not defined by the size of the sputtered contacts. It was therefore difficult to determine the exact number of tubes that were contacted without knowing the area of the probe tip that was in contact with the array. This problem can be avoided by using lithographically defined contacts as discussed in Chapter 5.

Finally, some time after the above measurements were performed, independent conductance measurements on the Y-junction CNT arrays using an STM tip were carried out [4.8]. Those measurements were also consistent with the results of this work.
Fig. 4.7. Y-junction CNT conductance data for different array samples. The measured currents are relatively low considering the gold pad contact size, indicating that the contacts are not continuous films.

4.3 Interpretation and Analysis of Results

The room temperature $I-V$ characteristics of the Y-junction CNTs are quite remarkable considering that only the diameter of the tubes changes on either side of the Y-junction structure: Measurements on straight multi-walled nanotubes have shown them to be semiconducting with a bandgap in the range of a few hundred meV that is inversely proportional to the diameter [4.9], which agrees with theoretical predictions for such tubes [4.10]. In addition, it has been shown that charge transport in non-metallic CNTs is dominated by hole transport at room temperature [2.22,2.27]. Field-effect experiments performed on straight nanotubes produced by the CVD method described in Chapter 3, also indicate that these multi-walled tubes are p-doped [4.11]. Thus the Y-junction CNTs were modeled as $p-p$ isotype semiconductor heterojunctions using standard heterostructure interface physics [4.12]. Sect. 4.3.1 describes the classic Anderson model for such heterojunctions, followed by a derivation of the governing electronic transport equations. In Sect. 4.3.2 the experimental Y-junction CNT conductance data is analyzed and compared to theory.
4.3.1 Anderson Model

Since the bandgap of semiconducting CNTs is inversely proportional to the diameter [2.7], the large bandgap side of the Y-junction corresponds to the narrow diameter "branch" tubes and the small bandgap side corresponds to the large diameter "stem" in the model (Fig. 4.8 (a)). At equilibrium, the Fermi level must be constant across the junction and this is accomplished by transfer of holes from the large bandgap side to the small bandgap side. The displacement of holes causes the bands to bend at the interface as shown in Fig. 4.8(a). Under applied forward bias (Fig. 4.8(b)) the Fermi level shifts, lowering the barrier to holes and allowing current to increase rapidly. Under reverse bias in these junctions, a small current flows and eventually the junction blocking collapses due to tunneling ("soft breakdown") [4.12]. This physical picture agrees qualitatively with the experimental results (Figs. 4.4, 4.5 and 4.7), with large current flowing under forward bias, defined as negative applied voltage, "pulling" positively charged holes across the junction. Under reverse bias (positive voltage) a small current is observed, and most junctions, both individually and in arrays, were observed to lose blocking between 3 to 4 V.

For a more quantitative picture, the standard Anderson approach is followed [4.13]: Assuming the applicability of Boltzmann statistics and making use of nanotube charge neutrality outside the junction region one can write Poisson's equation for the "stem" side of the heterojunction as [4.14] (k_B=1)

$$\epsilon_1 \frac{\partial^2 \bar{V}_1}{\partial x^2} = 4\pi q N_1 \left(1 - \exp \left[-q\bar{V}_1/T\right]\right);$$  \hspace{1cm} (1)

The "branch" side is considered to be almost depleted near the junction (Fig. 4.8(a)), allowing one to simplify it's Poisson equation to [4.12]

$$\epsilon_2 \frac{\partial^2 \bar{V}_2}{\partial x^2} = 4\pi q N_2;$$  \hspace{1cm} (2)
Fig. 4.8. Proposed p-p isotype heterojunction model for Y-junction CNT. (a) Band-edge diagram of junction in equilibrium; \( \Delta E_c \) and \( \Delta E_v \) represent the conduction and valence band energy offsets across the junction respectively. \( V_1' \) and \( V_2' \) are the built-in potential barriers to holes on the stem and branch sides of the junction respectively and \( E_F \) is the Fermi energy. The difference in bandgaps is given by \( \Delta E_g = \Delta E_c + \Delta E_v \). The wide bandgap side corresponds to the small diameter branches \( (D_2) \) and the narrow bandgap side to the larger diameter stem \( (D_1) \), as indicated schematically below the figure. \( N_1 \) and \( N_2 \) are the free hole carrier concentrations on either side of the junction far away from the transition region. (b) Junction under forward bias (dashed lines); the Fermi energy splits by \( eV_{\text{bias}} = e(V_1 + V_2) \), reducing the barrier to hole transport and allowing significant current to flow across the junction. (c) Logarithmic plot of \( I \) vs. \( V_{\text{bias}} \) for Y-junction CNT array data shown in Fig. 4.5(b) under large forward bias and linear fit to the experimental data. For the conductance data shown the fit gives \( \eta \sim 17 \) [4.13].

where \( \bar{V}_{1,2} = V_{1,2} - V_{1,2}' \), with \( V_{1,2} \) being the portions of the applied voltage \( V \) appearing in the stem (branch) sides of the junction, \( V_{1,2}' \) is the built-in potential barrier to hole flow on either side of the junction, \( N_{1,2} \) is the concentration of holes in the stem (branch) far...
from the junction, $\varepsilon_{1,2}$ is the corresponding dielectric constant, $q$ is the electronic charge, and $T$ is the thermodynamic temperature. Eq. (1) can be solved \[4.15\] yielding

$$\left| \frac{\partial \vec{V}_1}{\partial x} \right| = \left[ \frac{8\pi q N_1}{\varepsilon_1} \left[ \vec{V}_1 + \frac{T}{q} \left( \exp \left[ -\frac{q \vec{V}_1}{T} \right] - 1 \right) \right] \right]^{1/2}.$$  \tag{3}

Using the continuity condition across the junction interface ($\varepsilon_1 \vec{E}_1 = \varepsilon_2 \vec{E}_2$), under relatively large forward bias ($V_1 >> V'_1 >> T / q$, $V_2 >> V'_2$), Eqs. (2) and (3) result in the simple relation \[4.16\] ($V = V_1 + V_2$)

$$\varepsilon_2 N_2 V_2 = \varepsilon_1 N_1 (V - V_2).$$ \tag{4}

Furthermore, it follows from this model \[4.13\] that the current under large forward bias for these heterojunctions varies as

$$I \propto \exp \left[ q V_2 / T \right].$$ \tag{5}

Combining Eqs. (4) and (5) yields

$$I \propto \exp (q V / \eta T),$$ \tag{6}

where $\eta = 1 + \varepsilon_2 N_2 / \varepsilon_1 N_1$ is the junction parameter which depends only on the material properties on either side of the interface.

4.3.2 Data Analysis

In Fig. 4.8(c) a typical fit of the experimental Y-junction conductance data to the exponential dependence predicted by theory for large forward bias is shown. The data shows good agreement with the Anderson model. The utility of this model, assuming its
validity, goes beyond the \( I-V \) characteristics: From similar fits to the conductance data of both individual and array Y-junction samples \( \eta \) was found to lie in the range of 16 to 23. To extract further information about the Y-junction material properties the two limiting cases for the dielectric constant \( \varepsilon \) can be considered, i.e., low and high hole concentrations [4.17]: For low hole concentrations the linear fits give \( N_2/N_1 \) between 15 and 22, while the case of high hole concentration gives a range for \( N_2/N_1 \) between approximately 4 and 5. To assess which case may be more prevalent in Y-junction CNTs one can consider theoretical calculations based on a "self-doping" model [4.10] which predict \( D \gg a, \ a \) being the lattice constant

\[
\frac{N_2}{N_1} \sim \left[ \frac{D_1}{D_2} \right]^4
\]

(7)

for degenerately doped nanotubes [4.19]. For the diameters used in the experiments, this gives \( N_2/N_1 \) between 4 and 5, which implies that the free hole carriers may provide the dominant contribution to the dielectric constant [4.20]. However, both cases are consistent with the Y-junction tube structure in which the larger diameter stem tube \( D_1 \) resembles graphite and is therefore more lightly doped relative to the smaller diameter branches.

4.4 Summary and Discussion

The Y-junction CNT electrical transport characteristics presented in this chapter are robust and reproducible at room temperatures, from individual Y-junction tubes to many Y-junctions connected in parallel. One potential use of such nanoscale junctions is as very high-frequency diodes because of the small junction capacitance and minimal charge carrier storage effects. In addition, these results naturally lead the way to a 3-terminal heterojunction transistor-like device - the world's first transistor within a single molecular-scale structure. This can be realized using the same Y-junction structure by applying different voltages to each of the arms. Methods to separately contact the three arms of the Y-junction are currently being investigated (Chap. 5). More detailed models
of transport in the Y-junction tube should assess the effect of defects and disorder [4.21] and account for possible coherent effects in the junction region [4.22]. Nevertheless, it is intriguing that semiconductor heterojunctions, ubiquitous in conventional microelectronics, can be realized using nanometer scale Y-junction CNTs and that their behavior can be explained simply by considering the change in bandgap across the junction caused by joining together different diameter nanotubes.
References


[4.6] The lithographically patterned electrodes were prepared by Hope Chik.


[4.16] This result follows from equating the solutions to Eqs. (1) and (2) for the electric field at the junction interface ($x = x_0$) (Fig. 4.8(a)).

[4.17] For small hole concentrations, the dielectric constant is determined by a polarization term, making $\varepsilon$ independent of the free carrier concentration ($N$) [4.18]. On the other hand, for large hole concentrations a Drude-like contribution, $\varepsilon \propto N$, dominates the dielectric constant [4.18]. The former case gives $\eta = 1 + N_2 / N_1$, while the latter yields $\eta = 1 + (N_2 / N_1)^2$.


[4.20] References [2.22] and [2.27] measured relatively large hole carrier concentrations in straight CNTs of $\sim 10^7$/cm which provides further support for this interpretation.


5

Conclusion

The work presented in this thesis has dealt with the synthesis and properties of two new types of carbon nanotube structures; highly ordered arrays and Y-junctions. The key results of these efforts are listed in Sect. 5.1. Although these achievements are noteworthy, much work is still needed to better understand the physical properties of these novel nanostructures and allow the development of their practical applications. In Sect. 5.2 some ideas for future research are put forth and possible device applications based on the CNT arrays and Y-junctions are suggested. Finally, Sect. 5.3 brings this work to a close by providing an overview of the thesis from a more general perspective.

5.1 Summary

The main accomplishments of this thesis are summarized in Table 5.1. A representative list of journal publications and conference proceedings which resulted from this work is also shown.

5.2 Future Work

The accomplishments stated above lay a foundation for new areas of exploration on both pure and applied fronts. Possible pathways for future work on the synthesis, measurement and device applications of the novel carbon nanotube structures presented in this thesis are discussed below.
Table 5.1. Summary of Work

<table>
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<th>Accomplishment</th>
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5.2.1 Synthesis

On the NCA template front, although some work has been done [3.1, 3.15] further research is needed to understand the relationship between dependent variables such as the pore spacing, stem and branched pore diameters, branching angles, pore density and ordered domain size and externally controllable parameters such as cell voltage, temperature, and electrolyte composition and concentration. Additionally, it is important to understand the upper and lower limits of this template fabrication technique to determine for example, whether very small (<5 nm) diameter pores could be produced.
and if they can be ordered and/or branched. Further study into the pore branching mechanism is also required to understand the origin of this phenomenon [5.1]. Another challenge is to find the template branching parameters that permit the growth of branched carbon tubes, given that the energetically favoured geometry for pore branching may not be the same as that for branched tube growth. Growing alumina templates on different types and geometry of substrates has only recently begun to be explored [3.37] and further investigation into issues such as the required substrate conductivity and whether they can endure the chemical solutions and relatively high CNT growth temperatures used are required. Finally, other investigations should explore the utility of aluminum surface polishing as well as the use of single-crystal Al substrates to assess the influence of high-quality materials and crystal orientation on template properties. These questions have significant implications for the different types of highly ordered CNT array and Y-junction nanotube devices which may be fabricated using the NCA templates.

In terms of the CVD nanotube growth itself, further work is required to allow the controllable fabrication of CNT array structures for device applications. At this stage any explanation of the nanotube growth mechanism within NCA templates must remain speculative, however, it is likely that the NCA places a constraint on the catalytic decomposition of acetylene, forcing the tube structure to grow along the channel wall. Determining the exact nature of the growth process will require further detailed study. Compatibility between pore diameter and nanotube growth is another key issue to be studied: The influences which provide an as yet undetermined lower bound for the nanotube diameters need to be studied. In particular, the maximum nanotube length (pore depth) as a function of diameter should be influenced by the diffusion rates of reagents (C2H2) down the pore and byproducts (H2) up the pore. In addition, the effect of changing the amount and type of metal used at the pore bottoms and the total time of CVD growth, should be examined as well, to ascertain their effect on tube structure and quality. High temperature annealing to remove structural defects could also be attempted. Finally, the possibility of fabricating high-quality single-walled CNTs (straight and Y) in ordered arrays is an important goal.
Post-growth CNT removal from the template and purification are essential steps before performing device function tests on individual tubes. Unfortunately, the method described in Sect. 3.4.1 for obtaining CNT suspensions has some drawbacks, namely, the solution contains many unwanted carbon particles and there are a large amount of tube bundles rather than individual nanotubes. Different methods of purifying these solutions need to be developed and some possibilities include using electromigration [5.2] or template based filtration [5.3].

5.2.2 Measurements

The electronic transport experiments on CNTs grown within NCA templates can be improved to provide more stable contacts and allow temperature dependent measurements for both array and individual tube samples to be performed:

In the case of individual tubes dispersed on patterned electrodes, the step at the edge of the electrodes can be eliminated by depositing an additional oxide layer to fill the gap [4.4] as shown in Fig. 5.1. This will reduce tube bending across the electrode edge and also prevent tubes from getting trapped parallel to the metallic edges. In addition, by using wire-bonded contacts as opposed to probe tips, temperature dependent
Fig. 5.2. Two- and three-terminal configurations of Y-junction carbon nanotube electronic devices. The device on the left could be used as a molecular-scale diode (Chap. 4) while the three-terminal implementation (right) has the potential to be used as a molecular-scale transistor or switch by applying different voltages to each of the arms.

measurements can be performed using a cryostat. Methods for making separate contacts to the individual arms of the Y-junction CNTs should also be explored as this has the potential of allowing the first demonstration of a transistor based on a single nanotube structure (Fig. 5.2).

For electronic transport measurements through nanotube arrays on the other hand, it is desirable to eliminate any probe tip mechanical forces on the CNTs, which could damage the tube structure. This can be accomplished by using a lithographically patterned electrode surface on top of the array as shown in Fig. 5.3. This configuration also has the advantage of allowing a very precise measure of the number of tubes that are contacted. Forming the CNT array on a flat substrate such as a silicon wafer [3.37] would allow the reliable processing of such sample to be performed. In addition, by using a patterned electrode surface temperature dependent transport measurements are facilitated since the array can be wire-bonded without damaging the underlying nanotubes.
Fig. 5.3. Schematic of lithographically patterned electrode for measuring nanotube arrays. The metal contact is isolated from the rest of the array by an oxide film. An additional mask is then used to transfer a pattern of gold leads that connect the original metal contact to an area far from the CNTs being measured. In this way compressive forces on the nanotubes are eliminated.

5.2.3 Device Applications

The novel Y-junction carbon nanotubes and highly ordered nanotube arrays that were fabricated as part of this work create a rich environment for prospective device applications.

In terms of broad area devices, the arrangement, uniformity, and isolation of the CNTs embedded in the NCA matrix facilitates electrical contacting and further processing of the tube ends for device application based on the CNT arrays. One such application is infrared sensors based on Y-junction CNTs: The inherent asymmetry across the Y-junction region creates a nanoscale heterojunction as shown in Chapter 4. Since the narrow bandgap stem side can have a bandgap in the 100 meV range [5.4], these structures could be useful for infrared detection or imaging applications such as in spaced-based systems where the lightweight and inexpensive processes used would be well-suited. A schematic of the proposed device is shown in Fig. 5.4; The incoming radiation is incident on the wider bandgap branches of the array and is brought to the junction region where it is absorbed. This allows for efficient detection of radiation since the photons are not absorbed until they reach the heterojunction where the carrier concentration affects the current in an exponential fashion (Sect. 4.3.1). Such a device can be tuned to the desired wavelength by changing the tube diameters, and moreover,
since the template growth process is not inherently size-limited, very large panels of such devices could be inexpensively fabricated and used for imaging large areas in parallel. Another possible application is to use highly ordered straight CNT arrays for field-emission displays. In this case the excellent alignment of the nanotube tips should allow for efficient field emission and large arrays for thin film displays could be fabricated in a parallel process. Finally, the inherent electrical rectification in an array of Y-junction CNTs could be useful for high power diodes or perhaps even solar panels.

Turning now to devices using individual nanotubes, the possibility of nanotube-based electronics has been sought using straight nanotubes [2.22,2.27] and is now a goal for many in nanoelectronics [3.20]. The template grown Y-junction CNTs are the first example of molecular scale structures that could contain intrinsic transistor functionality. The thus far elusive goal of a three terminal molecular scale device would be large step towards making extremely complex and efficient circuits [1.12]. If three terminal Y-junction nanotube devices are realized the resulting molecular-scale transistors switches along with the already established diode operation [4.15], would represent a significant step towards developing future nanoelectronic circuits and systems. In addition, being able to integrate these individual nanodevices into high-density arrays using the NCA
template method is another unique feature of this approach and may allow connection to individual device elements using self-assembly methods [5.5].

Lastly, high-density memory and computational devices based on regular arrays of CNTs have recently shown much promise [5.6]. The highly ordered CNT arrays fabricated in this work may provide a cost-effective means of self-assembling such networks for future nanoelectronic building blocks based on periodic nanoarrays.

The above examples are merely a sampling of the many potential applications that exist for highly ordered CNT arrays and Y-junctions CNTs. Other possible areas of application include biotechnology, energy storage, chemical sensing and microfiltration (Chaps. 1 and 2).

### 5.3 Conclusion

This thesis has reported results on the fabrication of highly ordered carbon nanotube arrays and Y-junction carbon nanotubes; two new nanostructures which demonstrate the next step towards engineering nanotubes into functional materials promising for nanoscale science and technology: Electronic transport measurements of these structures were presented which showed that Y-junction nanotubes possess intrinsic rectifying behaviour at room temperature, representing a new type of semiconductor heterojunction - an important result for nanoelectronics. The future rewards of these investigations would appear to be even greater, foremost among them being the imminent possibility of using a Y-junction nanotube to demonstrate the world's first transistor within a single molecular-scale structure.

The work presented in this thesis has made significant advances to the field of carbon nanotubes, thereby contributing to the total nanotechnology effort (Chap. 1). Nanotechnology will undoubtedly require new ways of thinking to implement the many new possibilities it offers - most of which are just beginning to be explored. How
important nanotechnology will become remains to be seen, however, if the nanoscale is mastered, it may transform society and bring about a new, "nanomaterials age".
References


