

Carbon Nanotubes: Fabrication, properties and applications

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Abstract. Carbon nanotubes are in the forefront of nanomaterials research since their discovery last decade. These carbon molecules are tiny tubes with diameters down to 0.4 nm, while their lengths can grow up to a million times their diameter. In this paper the most common fabrication methods for Carbon Nanotubes are explained and their remarkable properties are portrayed, namely mechanical, electrical and electronic properties. Finally, some applications of Carbon Nanotubes based on the aforementioned properties are discussed.

Keywords: Nanotubes, Electric arc discharge, Laser ablation, Chemical vapour deposition, phonons.

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1. INTRODUCTION

In the past few years nanostructured materials, with dimensions of grain size, layer thickness or shapes, below 100 nm, are of special interest. This wide group of materials enables access to new ranges of electronic, magnetic, mechanical or optical properties. Polycrystalline materials with grain sizes less than a few nanometres possess properties different from classic materials, because they are relatively highly affected by the grain boundaries. For example they appear to be very strong and highly wear resistant coatings are being developed out of these materials. Furthermore, researchers at IBM used magnetic nanoparticles within several ultra-thin layers to develop advanced data storage devices. Sensors for disk-drives have been developed with many times the sensitivity of previous devices, allowing more bits to be packed on the surface of each disk. Nanoscale structures can potentially store trillions of bits of data per square inch, giving them a capacity 10 to 100 times greater than that of present memory devices.

Nanotubes belong to the promising group of nanostructured materials. Although nanotubes based on boron nitride and molybdenum are reported, Carbon Nanotubes (CNTs) are by far the most important group. These tubes contain one or several concentric graphite layers with diameters in the range of 0.4 nm up to tens of nanometres.

The discovery of the “buckyball”, i.e. a football shaped C₆₀ molecule, reported by Kroto et al. in 1985 [1], had a strong impact and marked the beginning of a new era in carbon material science. In 1991, Iijima discovered the carbon nanotube [2]. In the soot at the negative electrode of an arc discharge little tubes mixed with a large amount of other forms of carbon were found. Such multi-walled carbon nanotube (MWNT) contained 2 to 50 concentric cylindrical graphite sheets with a diameter of 3-10 nm and a length of up to 1 μm. This initial work led many groups throughout the world to produce and purify nanotubes. Soon it became clear that nanotubes have unique electronic and mechanical properties that are expected to lead to breaking industrial applications. Later on, single-walled carbon nanotubes (SWNT) were developed. Because of adhesive forces nanotubes often bunch to form ropes. The tubes can either be open-ended or have caps formed from half a C₆₀ molecule at either end, see Fig. 1.

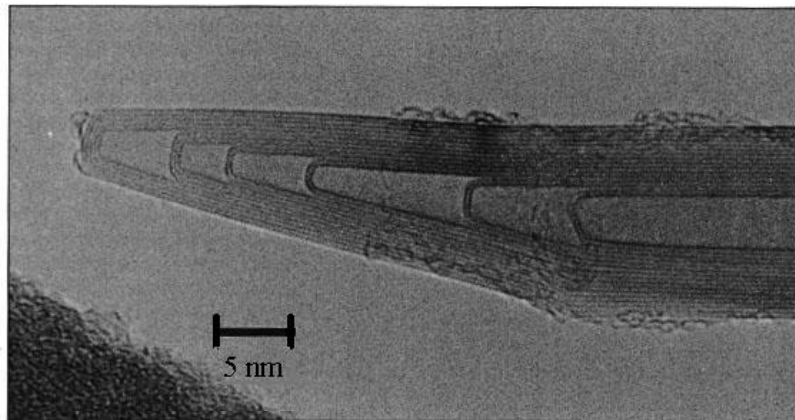


FIGURE 1. High resolution TEM image of the end of a typical nanotube showing several concentric layers with caps at the end.

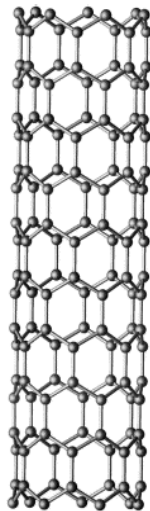


FIGURE 2. Ball-stick model of a nanotube; the balls represent the carbon atoms and the sticks their bonds [3].

To explain the carbon structure in nanotubes, the difference between diamond structure and that of graphite may be considered, see Figs. 2 and 3. In diamond, each carbon atom is attached with four others in a three dimensional lattice, which gives diamond its strength. On the other hand, in graphite, each carbon atom is attached to three others in a plane and form a hexagonal lattice, whilst the remaining bond is used to hold the planes above and below. The bonds in the plane are stronger than in diamond, but the interplanar bonds are relatively weak, and provide to the planes the possibility to slide. Therefore, whereas diamond is isotropic, graphite is anisotropic.

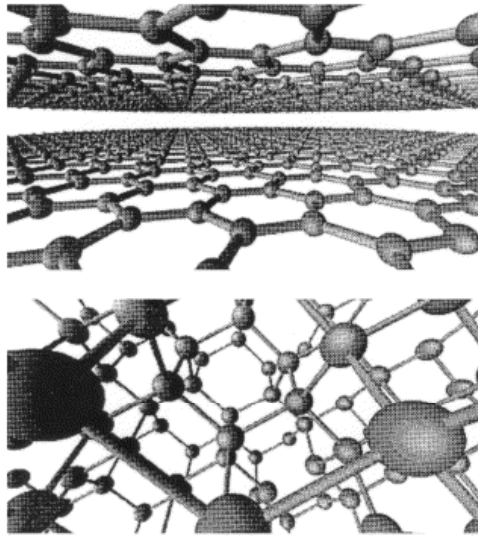


FIGURE 3. Differences between graphite (top) and diamond lattice (bottom) [3].

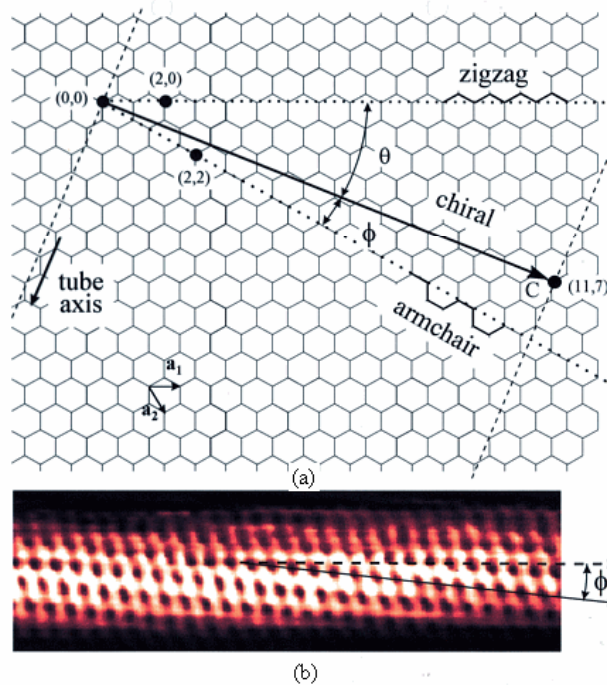


FIGURE 4. (a) The carbon lattice and the ways it can be rolled up to form a zigzag, an armchair or a chiral tube, depicted with its chiral angle; the atom at position (11,7) is projected on (0,0) like all the other atoms on the dotted line to form a tube. (b) STM image of the (11,7) chiral tube [5].

The structure of a nanotube is similar to that of graphite, with the difference that the sheets are closed to form a tube. In the ideal case, a CNT consists of either one cylindrical graphite sheet (single-walled nanotube) or several nested cylinders (multi-walled nanotube) with an interlayer spacing of 0.34-0.36 nm that is close to the typical spacing of graphite. The C-C bonds have a length of 0.14 nm, which is indeed shorter than the bonds in diamond, indicating that the material is even stronger than diamond [4]. Assuming that the a CNT is produced by the rolling of the hexagonal lattice, a few options exist. The sheet can be rolled-up along one of the symmetry axis, subsequently, either a zigzag tube or an armchair tube can be fabricated, see Fig. 4. It is also possible to roll-up the sheet in a direction that differs from a symmetry axis, therefore a chiral nanotube can be obtained. Besides the chiral angle, the circumference of the cylinder can also vary. By considering the rolling-up of the sheet as the “placement” of the atom at (0,0) on the atom at (n,m), tubes can be classified using this pair of integers, see Fig. 4; the roll-up vector (n,m) specifies the oriented width, recording the number of steps along the a and b directions.

2. CNTS FABRICATION

When heated, carbon atoms recombine in soot, some in amorphous blobs, but others in football-shaped spheres or in long cylindrical capsules. A notable progress has been made in the synthesis of these carbon nanotubes. In general, there are three ways to make soot that contains a reasonably high yield of nanotubes: electric arc discharge (EAD), laser ablation (LA) and chemical vapour deposition (CVD).

2.1 Electric arc discharge

The first identified nanotubes were fabricated by a direct current electric arc discharge (EAD) between carbon electrodes within a noble gas, like argon or helium [1, 6]. In this process, the carbon electrodes are placed a few millimetres apart and the current of approximately 100 A vaporises the carbon into hot plasma, some of which recondenses in the form of CNTs. Note that, the nanotubes form only where the current flows, i.e. on the larger negative electrode. The voltage of about 20 V, maintains a high temperature of 2000-3000 °C [7].

The typical yield of nanotubes is up to 30% by weight. The tubes have diameters between 2 and 20 nm and tend to be short, i.e. 50 µm or less, deposited in random sizes and directions; the typical rate of deposit is about 1 mm/min. It is to be noted that, an addition of a small amount of transition-metal powder, like cobalt, nickel or iron to the rods, favours the growth of single-walled nanotubes. The metal serves as a catalyst, preventing the growing tubular structures from wrapping around and closing into a smaller fullerene cage. The presence of a catalyst also allows for reducing the temperature. Without such cooling, the arc is too hot, and the nanotubes coalesce and merge rapidly into disorder; to minimise this effect a water-cooled cathode may be used [8].

2.2 Laser ablation

Single walled nanotubes (SWNT) can be efficiently produced by laser ablation (LA) of a graphite rod. These highly uniform tubes have a greater tendency to form aligned bundles than those prepared using arc-evaporation. With this method, SWNTs were generated consisting of CNTs, mostly of the armchair type, over 70% of the volume of material, bundled together into crystalline ropes of metallic character [9]. These ordered nanotubes are prepared by the laser

vaporisation of a carbon target in a furnace at 1100-1200 °C, a much lower temperature than was previously necessary for fabricating CNTs. A cobalt-nickel catalyst assists the growth of the CNTs, presumably because it prevents the ends from being “capped” during synthesis. By using two laser pulses, growth conditions can be maintained over a larger volume and for a longer time. This scheme provides more uniform vaporisation and better control of the growth conditions. The diameter range of the tubes can be controlled by varying the reaction temperature. Flowing argon or nitrogen gas sweeps the nanotubes from the furnace to a water-cooled copper collector placed just outside of the furnace. A disadvantage of this method is that it requires expensive lasers.

2.3 Chemical vapour deposition

Despite the described progress of synthetic techniques for nanotubes, there still remained two major problems in their synthesis, i.e. large scale and ordered synthesis. But, in 1996 a chemical vapour deposition (CVD) method emerged as a new candidate for nanotube synthesis [10]. The method was used to produce a 50 µm thick film of CNTs that were highly aligned perpendicular to the surface. This method is capable of controlling growth direction on a substrate and synthesising a large quantity of nanotubes. In this process a mixture of hydrocarbon gas, acetylene, methane or ethylene and nitrogen is introduced into the reaction chamber. During the reaction, nanotubes are formed on the substrate by the decomposition of hydrocarbon at temperatures 700-900°C at atmospheric pressure [11]. The process has two main advantages: the nanotubes are obtained at much lower temperature, although this is at the cost of lower quality, and the catalyst can be grown on a substrate, which allows for the formation of novel structures.

2.4 Purification of CNTs

The three different methods of the production of nanotubes suffer some serious limitations; all produce mixtures of nanotubes and nanoparticles sticking together in larger lumps. The tubes have a wide range of lengths, many defects and a variety of twists to them. Therefore, the main concern is how to separate them of the worthless soot and how to purify the tubes. Various post-growth treatments have been developed to purify the tubes and also to eliminate the defects in the tubes. The material can be treated in an ultrasonic bath to free many tubes from the particles that are originally stuck together [6]. The larger contaminants can be easily removed due to their relatively high weight, for example by dispersing the powder in a solvent and subsequent centrifugation. The smaller particles are more difficult to eliminate. One possibility for MWNTs is to perform an oxidative treatment, either by heating the powder in air at 650 °C or by a liquid phase treatment in acidic environment. For SWNTs, standard methods to eliminate catalyst particles and amorphous carbon involve re-fluxing the raw material in acid followed by centrifugation or cross-flow filtration.

Another possibility for purification is to employ physical methods that do not damage the tubes, but separate the objects as a function of their size. For MWNTs, a purification method that uses the properties of colloidal suspensions has been developed. Smaller objects remain dispersed while larger particles form aggregates that are deposited as sediment after a few hours. A related method, the size-exclusion chromatography, was successfully used for the purification and size selection for MWNTs. Purification procedures for SWNTs without any acidic treatment have also been reported and involve microfiltration or size-exclusion chromatography [4].

A method to eliminate the defects in CNTs is by annealing at high temperatures, up to 3000 K; during this process, impurities and defects in the tubes are eliminated.

3. CNTS PROPERTIES

CNTs exhibit properties that can find several uses and applications. Their mechanical, electrical and electronic properties will be hereafter discussed.

3.1 Mechanical properties

The mechanical properties of CNTs are difficult to be measured due to their small dimensions. However, different methods have been used. The Young's modulus of elasticity was estimated after measuring the thermal vibrations of nanotubes; a very high average value of 1.8 TPa was found [12]. Wong et al. [13] used a scanning force microscope to bend nanotubes that were mechanically fixed at one end. By measuring vibrations of nanotubes in an electrical field, Poncharal et al. [14] found a value below 1 TPa. This is true both for multi-walled and single-wall nanotubes because the modulus is mainly determined by the carbon-carbon bonds within the individual layers.

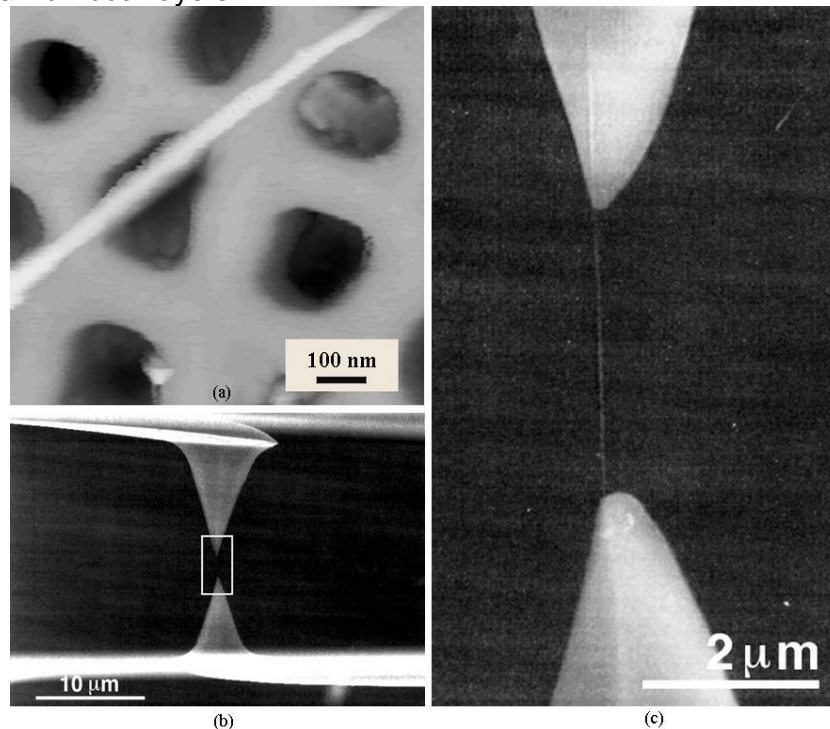


FIGURE 5. (a) An AFM microscope of a multi-walled nanotube across a pore to measure its Young's modulus by bending it with an AFM tip (b) and (c) SEM images of a multi-walled nanotube held between two AFM tips to measure its tensile strength.

Salvetat et al. [15] found that multi-walled nanotubes grown by arc discharge had a modulus of about 1 TPa, whereas those grown by the catalytic decomposition of hydrocarbons had a modulus that was smaller by one to two orders of magnitude. The nanotubes were placed across "nanopores" and an atomic force microscope was used to bend them in the middle. These results demonstrate that only highly ordered and well-graphitised nanotubes have a stiffness comparable to graphite, whereas those grown by catalytic decomposition are weaker because of their defects, see Fig. 5 (a) [15]. Further insights into the mechanical properties of multi-walled nanotubes are reported in Ref. [16]. The ends of a multi-walled nanotube were attached to a pair of AFM tips and stretched it until it broke, see Fig. 5 (b) and (c). The tips of the tubes were attached on the AFM tips by electron beam deposition of carbonaceous material. A

tensile strength of the nanotubes, ranged from 11 to 63 GPa was obtained; for comparison, high strength steel alloys break at about 2 GPa. The Young's modulus ranged from 270 to 950 GPa [16]. In this process, the AFM tips only make contact with the outside of the CNTs, so the outermost layer carries most of the load. The outermost tube ruptures at the tensile limit and slides over the inner tubes in the so-called "sword-in-sheath" failure. There are relatively weak Van der Waals interactions between the layers whilst the shear strength between the layers is small. This property is very interesting for applications like nano-bearings.

When nanotubes are compressed, they show remarkable properties. They bend over to surprisingly large angles, before they start to ripple and buckle, and then, finally kinks are developed. Note that all these deformations of the carbon nanotubes are elastic, all disappearing completely when the load is removed [16]. Note that the density of bundled CNTs is 1.33 to 1.40 gr/cm³; a very low value as compared to aluminium, possessing a density of 2.7 g/cm³ [8].

3.2 Electrical properties

Graphite is one of the rare materials known as a semimetal and CNTs emerge as interesting conductors. Because electron waves can reinforce or cancel one another, an electron spreading around the circumference of a nanotube can completely cancel itself out; therefore, only electrons with the right wavelength remain. From all the possible electron wavelengths, or quantum states, available in a flat graphite sheet, only a tiny subset is allowed when that sheet is rolled into a nanotube. That subset depends on the circumference of the nanotube, as well as on the chirality (twist) of the nanotube.

In a graphite sheet, one particular electron state, designated as the Fermi point, provides to the graphite almost its whole conductivity; none of the electrons in other states are free to move about. All armchair tubes and one out of three zigzag and chiral tubes combine the right diameter and degree of twist to include this special Fermi point in their subset of allowed states. These nanotubes are truly conducting metallic nanowires. The remaining two thirds of nanotubes are semiconductors. For example, if $n-m$ the roll-up factor, see Fig. 4, is three times an integer, the carbon nanotube has an extremely small gap, and at room temperature, it shows a metallic behaviour. For $n=m$, the tubes are metallic whilst for other values of $n-m$, the tubes behave as semiconductors with a band gap [5], indicating that, like silicon, they do not pass current easily without an additional amount of energy.

CNTs do not possess the same band gap, because for every circumference there is a unique set of allowed valences and conducting states; band gaps of 0.4-1 eV can be expected for SWNTs, corresponding to diameters between 0.6 and 1.6 nm [4]. As nanotube diameters increase, more and more states are allowed and the spacing between them reduces. In this way, different-size nanotubes can have band gaps as low as zero (like metal), as high as the band gap of silicon, and almost anywhere in between. No other known material can be so easily tuned. Note, however that, the growth of nanotubes currently provides a wide range of different geometries, and researchers are seeking improvements so that the specific types of nanotubes can be guaranteed.

Thick multi-walled nanotubes may display complex behaviour, because each layer of the tube has a slightly different geometry. By tailoring their composition individually, multi-walled tubes that are self-insulating or carry multiple signals at once, like nanoscopic coaxial cables, may be fabricated. However, the understanding and control of nanotube growth still falls short of these goals.

The fact that metallic nanowires are really good conductors is underlined by comparing them with copper. A bundle of nanotubes, could conduct about one billion A/cm² whilst copper wires about one million A/cm² [8].

3.3 Electronic properties

The electronic properties of single-walled carbon nanotubes are shown to be extremely sensitive to the chemical environment [17]. Exposure to air or oxygen dramatically affects the nanotubes resistance and other electronic properties. These parameters can be reversibly “tuned” by surprisingly small concentrations of adsorbed gases, and an apparently semiconducting CNT can be converted into an apparent metal through such exposure. Hence, the electronic properties of a given nanotube are not specified only by the diameter and chirality of the nanotube, but also depend critically on the gas exposure history.

Another very interesting electronic property of CNTs, is their field emission; they emit electrons from their tips, when they are placed in an electrical field, see Fig. 6 [18]. Because they are sharp, the nanotubes emit electrons at lower voltages than electrodes made from most other materials, and their strong carbon bonds allow nanotubes to operate for longer periods without damage.

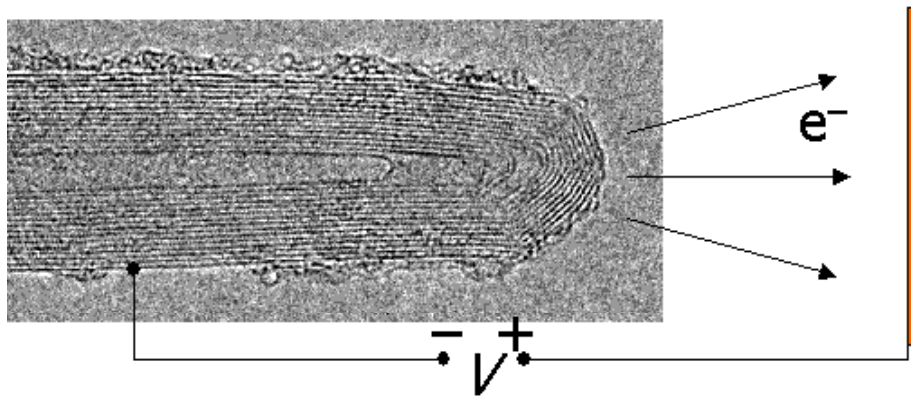


FIGURE 6. A schematic diagram of field emission of a nanotube.

3.4 Phonons and carriers in carbon nanotubes

The decoherence effects in low dimensional structures (e.g. CNTS) can be studied using the decoherence channels due to the Coulomb interaction to the background charge fluctuation and due to electron-phonon interaction [19]. The description of phonon modes are of special importance for estimating the *relaxation* and *dephasing* rates. Several models have been employed to calculate the phonon modes within CNTS like simple tight-binding model and the density-functional-based non-orthogonal tight-binding model among others [20]. On the other hand, the calculation of the carrier wavefunctions and the energy levels is subject of the numerical solution of Dirac equation.

Here, we briefly describe a semiclassical model of the dephasing mechanism. Neglecting the inhomogeneous broadening [21], the dephasing time (T_2) in terms of the excited-state lifetime T_1 and the pure-dephasing time T_2^* can be given by

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*}$$

The time T_2^* is related to the fluctuations in the carrier energy levels due to the interactions between the carriers and the phonons among others [19]. The corresponding dephasing and pure-dephasing time are a few tens of *fs*, while the relaxation time is a few tens of *ps* [21].

These kinds of calculations are very important for the quantum computer architecture and quantum optics research.

4 CNTS APPLICATIONS

The fact that nanotubes are very good conductors and that they also can appear as semiconductors or even insulators, makes them very useful for minuscule electronic devices like logic circuits built up out of several transistors. The making of tiny circuits might be promising for the semiconductor industry. This industry is focussed to make computer chips smaller every year, but also has to make them as cheap as possible.

Essential devices like field-effect transistors (FET) have been developed. They use a single semiconducting nanotube between two metal electrodes as the channel through which electrons flow. The current in this channel can be switched on or off by applying voltages to a nearby third “gate” electrode. It is found that this electrode can change the conductivity of the nanotube channel by a factor of one million or more, compared to silicon FETs. Because of its tiny size, however, the CNT-FET should switch reliably using much less power than a silicon-based device. It is predicted that, such a nanoscale device could run at clock speeds of one THz or more.

The fabrication of a CNT-FET starts with placing a tube on the insulating SiO₂ layer, by spincoating of a suspension, with pre-arranged conducting pads. These pads are connected with the tube by metal leads, lithographically deposited across the tube. This technique is designated as the four-probe technique [22]. The silicon layer below the silicon dioxide is used as the back gate. The first nanotube-based devices operated at very low temperatures, but in 1998 the first transistor was reported that worked at room temperature, with electrical characteristics remarkably similar to silicon devices, see Fig. 7 [23].

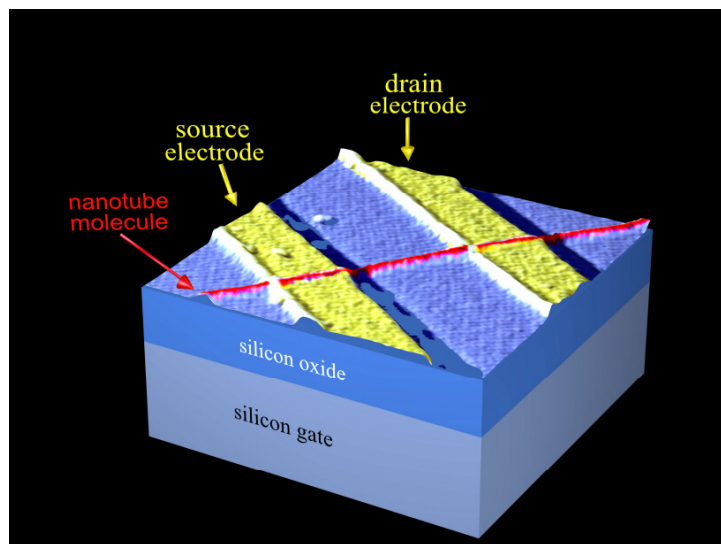


FIGURE 7. A single-molecule transistor that operates at room temperature, consisting of an individual semiconducting nanotube on two metal nanoelectrodes with the substrate as a gate electrode.

Metal-metal junctions lead to an improved version of a single electron transistor (SET). It has been proposed even as the future alternative to conventional silicon electronic components, but their practical use has been limited by the fact that they only operate at very low temperatures. However, recently the first single electron transistor operating at room temperature was reported

[24]. The device is similar to the FET described above, but with a short nanotube section of about 20 nm, that was manipulated by an atomic force microscope to create a Coulomb island. SETs consist of such a conducting island connected by tunnel barriers to two metallic leads. Strong bends (“buckles”) within the metallic carbon nanotubes are constructed using an AFM tip, and act as nanometre sized tunnel barriers for electron transport. The created resistance is in the order of 0.5 M Ω . For temperatures and bias voltages, that are low, relative to a characteristic energy required to add an electron to the island, electric transport through the device is blocked. Conduction or “Coulomb charging” is observed at room temperature, with an additional energy of 120 meV, by tuning a voltage on a close-by gate.

The next step in assessing the suitability of these devices for computer electronics involves the integration of individual CNT-FETs to form logic gates. To build such logic circuits, nanotube devices, that use electrons (n-type FET) and holes (p-type) as the carriers of electricity, are needed. The problem was that all CNT-FETs showed p-type characteristics, meaning that they were ON for negative gate bias [23]. Therefore, the first n-type CNT-FET had a great impact; it was made by direct doping of the tube with an electropositive element such as potassium. Potassium atoms (K atoms evaporated from an alkaline metal dispenser) are adsorbed onto the surface of the nanotube, donating electrons to convert the nanotube from p- to n-type. By covering half of the nanotube with PMMA, p-n junctions were produced [25]. Note, however, that, not only by doping, but also by annealing in a vacuum, their electrical character can be changed from p-type into n-type. Using vacuum annealing or doping to make n-type CNT-FETs, p- and n-CNT-FETs on the same substrate can be fabricated. These complementary CNT-FETs are assembled to form the first intermolecular logic gates. At first, a “NOT” gate or voltage inverter was demonstrated, see Fig. 8.

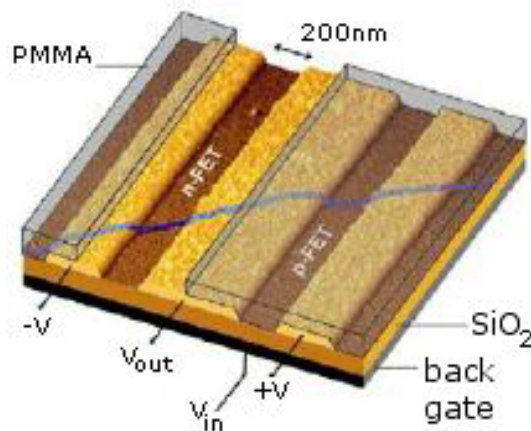


FIGURE 8. An AFM showing the design of an intramolecular logic gate consisting of a single nanotube bundle, positioned over the gold electrodes to produce two p-type CNT-FETs in series. The device is covered by PMMA, a window is opened by electron-beam lithography to expose part of the nanotube, and subsequently, potassium is evaporated through this window to produce an n-CNT-FET, while the other CNT-FET remains p-type [26].

Carbon fibre is already used to strengthen a wide range of materials, and the special properties of CNTs mean that they could be the ultimate high-strength fibre, which has a tensile strength 20 times, and a strength-to-weight ratio of 100 times that of steel. Nanotubes have already been used for reinforcement of nanostructural composite materials, polymers and concrete.

Incorporation of conducting carbon nanotubes in construction materials, such as concrete or structural plastics, provides opportunities for real time monitoring of material integrity and quality.

Open-ended nanostraws could penetrate into a cellular structure for chemical probing or could be used as ultrasmall pipettes to inject molecules into living cells. With the aid of computer simulations it was shown that water molecules will quickly enter and flow through a CNT of 8 nm in diameter. A separate set of simulations shows that certain organic molecules also will course through such nanotubes. The nanotubes conduct water at a rate similar to that of certain channels in the kidneys. These unusual transport properties of CNTs might be used in biomedical applications, such as highly targeted drug delivery.

The small size and sensitivity of nanotubes make the assembly of extremely powerful sensors possible. Semiconducting nanotubes change their electrical resistance dramatically when exposed to alkalis, halogens and other gasses at room temperature. For example, semiconducting CNTs have been used to detect gas molecules [27], whilst semiconductor nanowires have been used as detectors for a wide range of biological compounds. Also, nanowired field-effect transistors have been converted into sensors by modifying their surfaces with molecular receptors.

Kim and Lieber fabricated nanotube nanotweezers, by depositing free-standing electrically independent electrodes onto tapered glass micropipettes, which can be routinely made with end diameters of 100 nm [28]. The arms of the tweezers were about 4 μm long. The size of the nanotweezers was limited only by the optical microscope resolution used to monitor the attachment process.

5 CONCLUSIONS

In order to synthesise nanotubes there are three different methods, namely arc discharge, laser ablation, and CVD. For large-scale synthesis, the CVD method is most promising. The substrates can be recycled and the process works at lower temperatures (500–1000° C), which makes the process suitable for direct growth on several devices. Nanoparticles of a metal catalyst are applied to create nanotubes of better quality. Also the structure of the substrate is very important. It is shown that aligned pores in silicon and alumina are most suitable to create neatly aligned nanotubes. The deposition of the metal catalyst on the substrate deserves special attention, because it enables manipulated growth.

The strength (around 40 GPa) and stiffness (elastic modulus around 1 TPa) of nanotubes makes them suitable for reinforcing materials and ropes, which can bear high deformations, and extremely high tensile forces. The theoretical understanding of the electronic structure and related properties of nanotubes and their outstanding field emission properties have made them preferable for use in electronics.

Several applications of nanotubes have been proposed such as scanning probe tips, nanotweezers and even nanobearings and nanosprings. Nanotubes are commonly found in laboratories today, and research is stimulated by large amounts of money invested in it. Some companies are already specializing in the production of carbon nanotubes, and give research a boost.

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