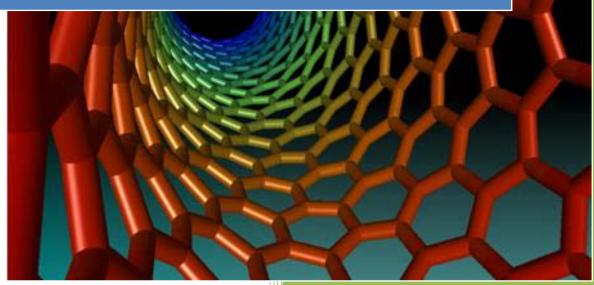
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Carbon Nanotubes – Seminar Report by Shuhab-u-Tariq – 1SI03EC109



Seminar Report by Shuhab-u-Tariq, 8th sem, E&C – UID: 1SI03EC109 Siddaganga Institute Of Technology 3/5/2007

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ABSTRACT

Nanotechnology is a field of applied science and technology covering a broad range of topics. The main unifying theme is the control of matter on a scale smaller than 1 micrometer, as well as the fabrication of devices on this same length scale. It is a highly multidisciplinary field, drawing from fields such as colloidal science, device physics, and supramolecular chemistry. Much speculation exists as to what new science and technology might result from these lines of research.

Nanotechnology and nanoscience got started in the early 1980s with two major developments; the birth of cluster science and the invention of the scanning tunneling microscope (STM). This development led to the discovery of fullerenes in 1985 and carbon nanotubes a few years later. Carbon nanotubes have recently received extensive attention due to their nanoscale dimensions and outstanding materials properties such as ballistic electronic conduction, immunity from electromigration effects at high current densities, and transparent conduction.

Since their discovery in 1991 by a Japanese scientist Sumio Iijima, **carbon-nanotubes** have been of great interest, both from a fundamental point of view and for future applications. The most eye-catching features of these structures are their electronic, mechanical, optical and chemical characteristics, which open a way to future applications. These properties can even be measured on single nanotubes. For commercial application, large quantities of purified nanotubes are needed.

Different types of carbon nanotubes can be produced in various ways. The most common techniques used nowadays are: arc discharge, laser ablation, chemical vapour deposition and flame synthesis.

Many of the extraordinary properties attributed to nanotubes—among them, superlative resilience, high electrical conductivity, high ductility, high tensile strength, thermal stability and relative chemical inactivity —have fed fantastic predictions of microscopic robots, dent-resistant car bodies and earth-quake-resistant buildings. The above characteristics have generated strong interest in their possible use in nano-electronic and nano-mechanical devices. For example, they can be used as nano-wires or as active components in electronic devices such as the field-effect transistors.

Fundamental and practical nanotube researches have shown possible applications in the fields of energy storage, molecular electronics, nanomechanic devices, and composite materials.

CARBON NANOTUBES

Introduction:

Carbon comes from a Latin word "*carbo*", which is derived from a French word "*charbon*", meaning charcoal. It is the fourth most abundant chemical element in the universe by mass, after hydrogen, helium, and oxygen.

The allotropes of carbon are the different molecular configurations that pure carbon can take. Allotropes of carbon include Diamond, Graphite, Amorphous carbon, Fullerenes, Carbonnanotubes, Carbon-nanobuds, Aggregated diamond nanorods, Glassy carbon, Carbon nanofoam, Lonsdaleite & Chaoite.

What are Carbon-nanotubes...?

Carbon-nanotubes (CNTs) are allotropes of carbon. These are extremely thin hollow cylinders made of carbon atoms.

A <u>carbon nanotube</u> is a one-atom thick sheet of graphite (called graphene) rolled up into a seamless cylinder with diameter of the order of a nanometer. This results in a nanostructure

where the length-to-diameter ratio exceeds 10,000. Such cylindrical carbon molecules have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Nanotubes are members of the fullerene structural family.

The **fullerenes**, discovered in 1985 by researchers at Rice University, are a family of carbon allotropes named after Richard Buckminster Fuller and are sometimes called **buckyballs**. They are molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Cylindrical fullerenes are called **Carbon nanotubes** or **buckytubes**. Fullerenes are similar in structure to graphite, which is composed of a sheet of linked hexagonal rings, but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. A nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is of the order of a few nanometres (approx.10,000 to 50,000 times smaller than the width of a human hair), while they can be upto several millimetres in length.

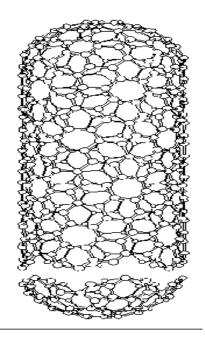


Fig: Single-walled CNT

Nanotubes are cylindrical fullerenes. These tubes of carbon are usually only a few nanometres wide, but they can range from less than a micrometre to several millimetres in length. They often have closed ends, but can be open-ended as well. There are also cases in which the tube reduces in diameter before closing off. Their unique molecular structure results in unique macroscopic properties, including high tensile strength, high electrical conductivity, high ductility, high resistance to heat, and relative chemical inactivity as it is round with no exposed atoms that can be easily displaced, such as in Benzene. They have the ability to be either metallic or semiconducting depending on the "twist" of the tube.

There are two main types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

The nature of the bonding of a nanotube is described by applied quantum chemistry, specifically, orbital hybridization. Nanotubes are composed entirely of sp^2 bonds, similar to those of graphite. This bonding structure, which is stronger than the sp^3 bonds found in diamond, provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by Vander-Waals forces. Under high pressure, nanotubes can merge together, trading some sp^2 bonds for sp^3 bonds, giving great possibility for producing strong, unlimited-length wires through high-pressure nanotube linking.

Classification of Carbon Nanotubes

Based on Conductivity:

- o Metallic
- o Semiconducting

Based on Chirality:

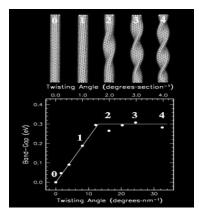
- o Zigzag
- o Armchair
- o Chiral

Based on layers:

- Single walled nanotubes (SWNT)
- o Multi walled nanotubes (MWNT)

1. Classification based on Conductivity:

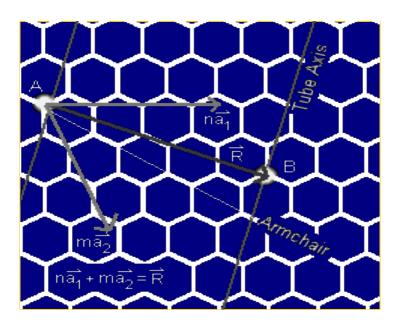
The conductance of a carbon-nanotube is mainly affected by its chirality (amount of twist in the tube). Twisting is found to transform the metallic nanotube to a semiconducting one with a band-gap that varies with the twist angle as shown below.



Carbon nanotubes display either metallic or semiconducting properties. Both large, multiwalled nanotubes (MWNTs), with many concentric carbon shells, and bundles or ropes of aligned single-walled nanotubes (SWNTs) are complex composite conductors that incorporate many weakly coupled nanotubes that each have a different electronic structure. Carbon nanotubes exhibit several technologically important characteristics. Metallic (m) nanotubes can carry extremely large current densities; semiconducting (s) nanotubes can be electrically switched on and off as field-effect transistors (FETs). The two types may be joined covalently.

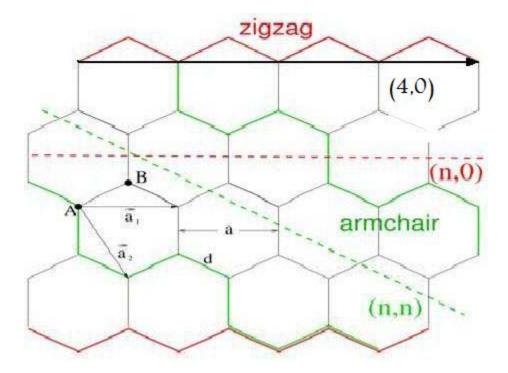
2. Classification based on Chirality:

CNTs based on their chirality are classified as Zig-Zag, Armchair and Chiral.



Nanotubes form different types, which can be described by the chiral vector (n, m), where n and m are integers of the vector equation $\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$. The chiral vector is determined as shown in the diagram. Imagine that the nanotube is unraveled into a planar sheet. Draw two lines (the blue lines) along the tube axis where the separation takes place. In other words, if you cut along the two blue lines and then match their ends together in a cylinder, you get the nanotube that you started with. Now, find any point on one of the blue lines that intersects one of the carbon atoms (point A). Next, draw the Armchair line (the thin yellow line), which travels across each hexagon, separating them into two equal halves. Now that you have the armchair line drawn, find a point along the other tube axis that intersects a carbon atom nearest to the Armchair line (point B). Now connect A and B with our chiral vector, R (red arrow). The wrapping angle (not shown) is formed between R and the Armchair line.

If R lies along the Armchair line ($\Phi=0^\circ$), then it is called an "**armchair**" nanotube. If $\Phi=30^\circ$, then the tube is of the "**zigzag**" type. Otherwise, if $0^\circ < \Phi < 30^\circ$ then it is a "**chiral**" tube. The vector a_1 lies along the "zigzag" line. The other vector a_2 has a different magnitude than a_1 , but its direction is a reflection of a_1 over the Armchair line. When added together, they equal the chiral vector R.



The values of n and m determine the chirality, or "twist" of the nanotube. The chirality in turn affects the conductance of the nanotube, it's density, it's lattice structure, and other properties. A SWNT is considered metallic if the value n - m is divisible by three. Otherwise, the nanotube is semiconducting, i.e.

If (n - m) / 3 = 0, the tube is metallic

If $(n - m) / 3 \neq 0$, the tube is semiconductor

Consequently, when tubes are formed with random values of n and m, we would expect that twothirds of nanotubes would be semi-conducting, while the other third would be metallic, which happens to be the case.

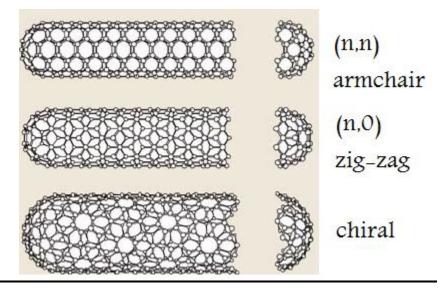


Fig: Classification based on chirality: n=m (armchair), m=0(zig-zag), otherwise chiral.

3. Classification based on Layers:

Carbon nanotubes are an outgrowth of the formation of carbon fullerenes, such as the C60 buckyball molecule. There are two basic types of nanotubes. Singlewalled nanotubes (SWNTs) have one shell of carbon atoms in a hexagonal arrangement.

Multiwalled nanotubes (MWNTs) consist of multiple concentrically nested carbon tubes.

Single-walled nanotubes

Most single-walled nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that can be many thousands of times longer. Single-walled nanotubes with length up to orders of centimeters have been produced.



Figure : Scanning electron micrograph of single-walled carbon nanotubes grown with the high-pressure carbon monoxide process. (Antenna Group, Nanomix, Inc.)

In 2004, scientists from University of California have recently grown a world record-length fourcentimeter-long, single-walled carbon nanotube.

The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n,m) called the chiral vector. The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If m=0, the nanotubes are called "zigzag". If n=m, the nanotubes are called "armchair". Otherwise, they are called "chiral".

Single-walled nanotubes are a very important variety of carbon nanotube because they exhibit important electric properties that are not shared by the multi-walled carbon nanotube (MWNT) variants. Single-walled nanotubes are the most likely candidate for miniaturizing electronics past the micro electromechanical scale that is currently the basis of modern electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors.

One useful application of SWNTs is in the development of the first intramolecular field effect transistors (FETs). The production of the first intramolecular logic gate using SWNT FETs has recently become possible as well. To create a logic gate you must have both a p-FET and an n-FET. Because SWNTs are p-FETs when exposed to oxygen and n-FETs when unexposed to oxygen, they were able to protect half of a SWNT from oxygen exposure, while exposing the

other half to oxygen. The result was a single SWNT that acted as a NOT logic gate with both p and n-type FETs within the same molecule.

Single-walled nanotubes are still very expensive to produce (the cost is about \$1,500 per gram) and the development of more affordable synthesis techniques is vital to the future of carbon nanotechnology. If cheaper means of synthesis cannot be discovered, it would make it financially impossible to apply this technology to commercial-scale applications.

Multi-walled nanotubes

Multiwalled nanotubes (MWNT) consist of multiple layers of graphite rolled in on themselves to form a tube shape.

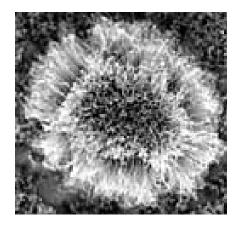


Figure : Scanning electron micrograph of mutliwalled carbon nanotubes grown with chemical vapor deposition. (Antenna Group, Nanomix, Inc.)

There are two models which can be used to describe the structures of multiwalled nanotubes. In the *Russian Doll* model, sheets of graphite are arranged in concentric cylinders, eg a (0,8) single-walled nanotube (SWNT) within a larger (0,10) single-walled nanotube. In the *Parchment* model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper. The interlayer distance is close to the distance between graphene layers in graphite.

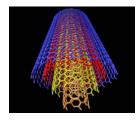


Fig: Multi-walled nanotube

The special place of Double-walled Carbon Nanotubes (DWNT) must be emphasized here because they combine very similar morphology and properties as compared to SWNT, while improving significantly their chemical resistance. This is especially important when functionalisation is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT.

In the case of SWNT, covalent functionalisation will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003 by the CCVD technique, from the selective reduction of oxides solid solutions in methane and hydrogen.

Each type has its advantages and disadvantages. MWNTs are easier and less expensive to produce because current synthesis methods for SWNTs result in major concentrations of impurities that require removal by acid treatment. But MWNTs have a higher occurrence of structural defects, which diminishes their useful properties.

Properties of Carbon-nanotubes

<u>Size:</u> C-nanotubes are extremely thin hollow cylinders made of carbon atoms. There size ranges from about 0.6 to 1.8 nanometers in diameter.

Density: 1.33 to 1.40 grams per cubic centimetre. To make a comparison, Aluminum has a density of 2.7 grams per cubic centimetre.

<u>Current carrying capacity</u>: The current carrying capacity of SWCNTs is estimated at 1 billion amperes per square centimeter. Copper wires burn out at about 1 million ampere per square centimeter.

<u>Resilience</u>: C-nanotubes can be bent at large angles and restraightened without damage.

<u>Strength</u>: Carbon nanotubes are one of the strongest and stiffest materials known, in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 GPa. SWCNTs have an average tensile strength of

about 45 GPa(45 billion pascals). In comparison, high-carbon steel has a tensile strength of approximately 1.2 GPa and other high-strength steel alloys break at about 2 billion Pa. CNTs have very high elastic modulus, on the order of 1 TPa.

<u>Kinetic</u>: Multiwalled carbon nanotubes, multiple concentric nanotubes precisely nested within one another, exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell thus creating an atomically perfect linear or rotational bearing. This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. Already this property has been utilized to create the world's smallest rotational motor and a nanorheostat. Future applications such as a gigahertz mechanical oscillator are also envisaged.

Electrical: Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n,m) nanotube, if n - m is a multiple of 3, then the nanotube is metallic, otherwise the nanotube is a semiconductor. Thus all armchair (n=m) nanotubes are metallic, and nanotubes (5,0), (6,4), (9,1), etc. are semiconducting. In theory, metallic nanotubes can have an electrical current density more than 1,000 times greater than metals such as silver and copper.

Thermal: All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction," but good insulators laterally to the tube axis. It is predicted that carbon nanotubes will be able to transmit heat up to 6000 watts per meter per kelvin at room temperature; compare this to copper, a metal well-known for its good thermal conductivity, which only transmits 385 W/m/K. The temperature stability of carbon nanotubes is estimated to be up to 2800 degrees Celsius in vacuum and about 750 degrees Celsius in air.

Defects: As with any material, the existence of defects affects the material properties. Defects can occur in the form of atomic vacancies. High levels of such defects can lower the tensile strength by up to 85%. Another well-known form of defect that occurs in carbon nanotubes is known as the Stone Wales defect, which creates a pentagon and heptagon pair by rearrangement of the bonds. Because of the very small structure of CNTs, the tensile strength of the tube is

dependent on the weakest segment of it in a similar manner to a chain, where a defect in a single link diminishes the strength of the entire chain.

The tube's electrical properties are also affected by the presence of defects. A common result is the lowered conductivity through the defective region of the tube. Some defect formation in armchair-type tubes (which are metallic) can cause the region surrounding that defect to become semiconducting. Furthermore single monoatomic vacancies induce magnetic properties.

The tube's thermal properties are heavily affected by defects. Such defects lead to phonon scattering, which in turn increases the relaxation rate of the phonons. This reduces the mean free path, and reduces the thermal conductivity of nanotube structures.

Synthesis of C-nanotubes

Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high pressure carbon monoxide (HiPco),

and chemical vapour deposition(CVD). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can take place in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

Arc discharge

Nanotubes were observed in 1991 in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100amps, that was intended to produce fullerenes. Because nanotubes were initially discovered using this technique, it has been the most widely used method of nanotube synthesis.

The carbon arc discharge method, initially used for producing C60 fullerenes, is the most common and perhaps easiest way to produce carbon nanotubes as it is rather simple to undertake. However, it is a technique that produces a mixture of components and requires separating nanotubes from the soot and the catalytic metals present in the crude product.

This method creates nanotubes through arc-vaporisation of two carbon rods placed end to end separated by approximately 1mm, in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). Recent investigations have shown that it is also possible to create nanotubes with the arc method in liquid nitrogen. A direct current of 50 to 100 A driven by

approximately 20 V creates a high temperature discharge between the two electrodes. The discharge vaporises one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode.

The yield for this method is up to 30 percent by weight and it produces both single- and multiwall nanotubes, however they are quite short (50 microns).

Laser Ablation

In the laser ablation process, a pulsed laser vaporizes a graphite target in a high temperature reactor while an inert gas is bled into the chamber. The nanotubes develop on the cooler surfaces of the reactor, as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes. This method has a yield of around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition.

Chemical Vapour Deposition

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by deposition of a transition metal (Co.Ni.Fe) onto a substrate (SiO₂, Zeolite, MCM, Metal Oxide, Al_2O_{3}) and then using different sources of carbon (CH₄C₂ H ₂, C₂H₄, CO) for decomposition of carbon, finally the products are purified by different methods such as Oxidation, Acid treatment, Annealing, Ultra Sonication, Magnetic purification, micro filtration, cutting, functionalisation and chromatography. Typical yields for CVD are approximately 30 percent.

At the moment, laser ablation method produces the cleanest material, but the costs are still rather high. Arc discharge can produce grams of low purity nanotubes. The CVD technique is still under development but preliminary results look promising, as do prospects of large scale CVD.

Natural, incidental, and controlled flame environments

Fullerenes and carbon nanotubes are not necessarily products of high-tech laboratories; they are commonly formed in such mundane places as ordinary flames, produced by burning methane, ethylene, and benzene, and they have been found in soot from both indoor and outdoor air. However, these naturally occurring varieties can be highly irregular in size and quality because the environment in which they are produced is often highly uncontrolled. Thus, although they can be used in some applications, they can lack in the high degree of uniformity necessary to meet many needs of both research and industry. Recent efforts have focused on producing more uniform carbon nanotubes in controlled flame environments.

Applications of Carbon Nanotubes

"The Next Big Thing Is Really Small"

Since their discovery in 1991, researchers have envisioned carbon nanotubes as the most viable candidates to dominate the coming 21st century revolution in nanotechnology. Barely a decade old, these unique materials are already in use in lithium-ion batteries, as structural reinforcements, and in flat-panel displays using nanotube components as field emitters. Other potential applications in development include <u>chemical sensors</u>, probe tips, fuel cells, portable X-ray machines, extremely lightweight and strong fabrics, artificial muscles, and components that will dramatically reduce the weight of cars and spacecraft. It's expected that Carbon nanotechnology in this century will impact almost every aspect of our lives. The only question is, when? "The answer depends on our ability to fabricate nanotechnology materials more easily than is possible now, and turning them into useful products."

The size, strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering.

Nanotubes can be either electrically conductive or semiconductive, depending on their helicity, leading to nanoscale wires and electrical components. These one-dimensional fibers exhibit electrical conductivity as high as copper, thermal conductivity as high as diamond, strength 100 times greater than steel at one sixth the weight, and high strain to failure.

Many potential applications have been proposed for carbon nanotubes, including <u>conductive and</u> <u>high-strength composites; energy storage</u> and energy conversion devices; <u>sensors; field emission</u> <u>displays</u> and radiation sources; <u>hydrogen storage media</u>; and <u>nanometer-sized semiconductor</u> <u>devices, probes & interconnects</u>. Some of these applications are now realized in products.

Energy Storage

Graphite, carbonaceous materials and carbon fibre electrodes are commonly used in fuel cells, batteries and other electrochemical applications. Advantages of considering nanotubes for energy storage are their small dimensions, smooth surface topology and perfect surface specificity. The efficiency of fuel cells is determined by the electron transfer rate at the carbon electrodes, which is the fastest on nanotubes following ideal Nernstian behaviour. Two elements that can be electrochemically stored in CNTs are hydrogen and lithium.

Hydrogen storage

The advantage of hydrogen as energy source is that its combustion product is water. In addition, hydrogen can be easily regenerated. For this reason, a suitable hydrogen storage system is necessary, satisfying a combination of both volume and weight limitations. The two commonly used means to store hydrogen are gas phase and electrochemical adsorption.

Because of their cylindrical and hollow geometry, and nanometre-scale diameters, it has been predicted that carbon nanotubes can store a liquid or a gas in the inner cores through a capillary effect.

Most experimental reports of high storage capacities are rather controversial so that it is difficult to assess the applications potential. What lacks, is a detailed understanding of the hydrogen storage mechanism and the effect of materials processing on this mechanism. Another possibility for hydrogen storage is electrochemical storage. In this case not a hydrogen molecule but an H atom is adsorbed. This is called chemisorption.

Electrochemical supercapacitors

Supercapacitors have a high capacitance and potentially applicable in electronic devices. Typically, they are comprised two electrodes separated by an insulating material that is ionically conducting in electrochemical devices. The capacity of an electrochemical supercap inversely depends on the separation between the charge on the electrode and the counter charge in the electrolyte. Because this separation is about a nanometre for nanotubes in electrodes, very large capacities result from the high nanotube surface area accessible to the electrolyte. In this way, a large amount of charge injection occurs if only a small voltage is applied. This charge injection is used for energy storage in nanotube supercapacitors. Generally speaking, there is most interest in the double-layer supercapacitors and redox supercapacitors with different charge-storage modes.

Molecular Electronics with CNTs

It's a matter of fact that the miniaturisation of silicon devices is going to reach the fundamental quantum-type limits in a near future, and a lot of effort is being done in the research of pursuing this minuaturisation further than the limit of the ultimate MOS transistor. In this context, Molecular Electronics is a relatively recent scientific discipline which uses individual or grouped molecules in order to realize electronic functions. For that purpose, Carbon-nanotubes are macromolecular entities with physical properties that should enable the realization of Molecular Electronics at the scale of the Electronics Industry.

Field emitting devices

If a solid is subjected to a sufficiently high electric field, electrons near the Fermi level can be extracted from the solid by tunnelling through the surface potential barrier. This emission current depends on the strength of the local electric field at the emission surface and its work function (which denotes the energy necessary to extract an electron from its highest bounded state into the vacuum level). The applied electric field must be very high in order to extract an electron. This condition is fulfilled for carbon nanotubes, because their elongated shape ensures a very large

field amplification. For technological applications, the emissive material should have a low threshold emission field and large stability at high current density. Furthermore, an ideal emitter is required to have a nanometre size diameter, a structural integrity, a high electrical conductivity, a small energy spread and a large chemical stability. Carbon nanotubes possess all these properties. However, a bottleneck in the use of nanotubes for applications is the dependence of the conductivity and emission stability of the nanotubes on the fabrication process and synthesis conditions.

Examples of potential applications for nanotubes as field emitting devices are flat panel displays, gas-discharge tubes in telecom networks, electron guns for electron microscopes, AFM tips and microwave amplifiers.

X Rays to Go: Carbon nanotubes could shrink machines

Carbon-nanotubes have found their way into a novel X-ray machine that could improve examinations of patients in the hospital, victims at the scene of an automobile crash, or luggage at airport-security checkpoints.

Unlike conventional machines, the new one doesn't require high temperatures to generate highenergy electrons for producing X rays. A thin layer of carbon nanotubes operating at room temperature are used to generate high-energy electrons instead, says developer Otto Zhou of the University of North Carolina at Chapel Hill.

A conventional X-ray machine generates electrons by heating metal filaments inside a vacuum chamber to temperatures as high as 2,000°C. When those electrons hit another piece of metal, they produce X rays. The prototype devised by Zhou and his colleagues uses carbon nanotubes in place of the metal filaments. When exposed, unheated, to an electric field, the nanotubes behave like tiny electron guns.

Since metal filaments burn out easily at their high operating temperatures, the new devices will last longer. They should also save energy and time. Moreover, because the prototype operates at room temperature, researchers will be able to develop very small machines for portable X-ray work, such as in an ambulance or airport-security and customs operations.

This important work brings carbon-nanotube X-ray sources much closer to commercializable products. X-ray sources based on carbon nanotubes might even be small enough someday for use in catheters inserted into the body.

A new family of technologies using similar methods might become possible. This X-ray application is one of the many exciting potential uses of carbon nanotubes as electron sources, from light-emitting flat-panel displays and high-intensity lamps to microwave generators and electrical-discharge tubes for electrical-surge protection.

Nanotube flat display devices

One of the many promising types of applications for carbon nanotubes is flat electronic display devices. In 1997, a joint research team from the National Institute of Materials and Chemical Research and Mie University discovered that carbon nanotubes emit ring-shaped electron discharges when they are exposed to a weak electrical field. The ring-shaped discharges are nanometer sized and are emitted from the ends of the tubes. In 1999, Ulvac Japan Ltd developed a process for growing carbon nanotubes which are both aligned vertically and located at the desired locations on base plates of field emission displays (FED). (FEDs are a new type of flat panel display device which is currently being developed. They combine the high image quality of CRT with the thinness and low power consumption of LCD).

Transistors

Carbon nanotubes can in principle play the same role as silicon does in electronic circuits, but at a molecular scale where silicon and other standard semiconductors cease to work. Although the electronics industry is already pushing the critical dimensions of transistors in commercial chips be-low 200 nanometers (billionths of a meter)—about 400 atoms wide—engineers face large obstacles in continuing this miniaturization. Within this decade, the materials and processes on which the computer revolution has been built will begin to hit fundamental physical limits. Still, there are huge economic incentives to shrink devices further, because the speed, density and efficiency of microelectronic devices all rise rapidly as the minimum feature size decreases. Experiments over the past several years have given researchers hope that wires and functional devices tens of nanometers or smaller in size could be made from nanotubes and incorporated into electronic circuits that work far faster and on much less power than those existing today.

Transistors are the basic building blocks of integrated circuits. To use nanotubes in future circuits it is essential to be able to make transistors from them.

Carbon Nanotube Transistors exploit the fact that nm-scale nanotubes are ready-made molecular wires and can be rendered into a conducting, semiconducting, or insulating state, which make them valuable for future nanocomputer design.

The gain of CNT-transistors is 10 - 100 times that of the silicon transistors used for present day integrated circuits, and thus they hold promise as the next generation of transistors.

The electrical characteristics of nanotube-FETs have been measured and the results show that the amount of current (I_{SD}) flowing through the nanotube channel can be changed by a factor of 100,000 by changing the voltage applied to gate (V_G).

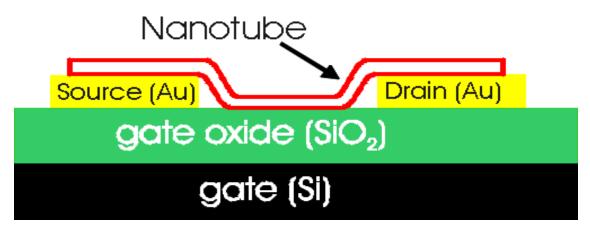
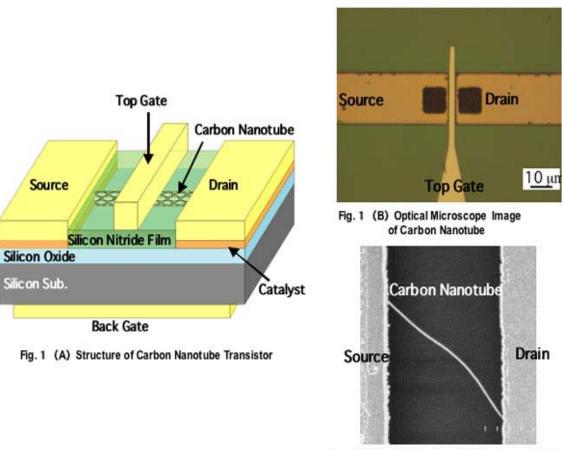


Diagram of a conventional CNT-FET (IBM Nanoscience Department)

However, these conventional CNT-FETs have crucial disadvantages in transistor characteristics in that the electric current significantly fluctuates with time, sometimes resulting in current variations of several tens %. In addition, their current-voltage characteristics exhibit a hysteresis, that is, the current value is not uniquely determined by the applied voltage value, but depends on the history of the voltage change. For this reason, CNT-FETs can not be used in practical applications. Stable CNT-FETs have been strongly desired for practical use. The cause of the transistor instability was considered to be due to water and oxygen adsorbed on the CNT surface, but even when they were completely removed from the surface, characteristics stable enough for practical use could not be achieved.

The Institute of Scientific and Industrial Research (Osaka University), the National Institute of Advanced Industrial Science and Technology (AIST), and Japan Science and Technology Agency have jointly succeeded in investigating the cause of the instability of conventional CNT-FETs, and further development of a production process for a new carbon nanotube transistor (CNT transistor), and thereby succeeded in the development of a CNT transistor with an operational stability 1000 or more times that of conventional CNT transistors.

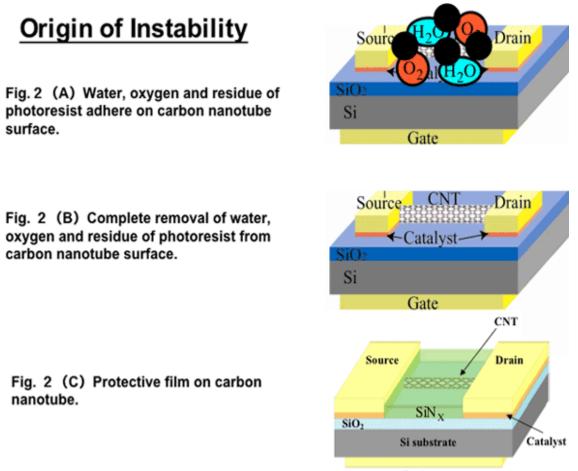


Structure of Carbon Nanotube Transistor

Fig. 1 (C) Scanning Electron Microscope Image of Carbon Nanotube

Figure 1(A) shows a structural illustration of a CNT-FET, in which the CNTs are formed on a silicon oxide thin film/silicon substrate, and source- and drain-electrodes, made of metal, are formed on both ends of the CNT region to take out the electric current. Furthermore, it should be noticed that the surface of the CNTs are covered with a silicon nitride thin film. Furthermore, on

the silicon nitride thin film, the top gate electrode, being capable of controlling the electric current flowing in the CNTs, is formed. On the rear side of the silicon substrate, the back gate, similarly controlling the electric current, is formed. Figure 1(B) shows an optical microscopic image of a CNT-FET. In this image, each metallic electrode is visible, while the CNTs are not visible, because they are formed under the gate electrode. Figure 1(C) shows a scanning electron microscopic image of a CNT between the electrodes.

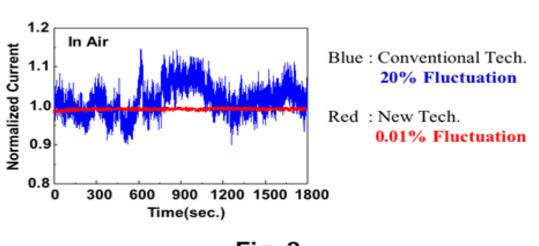


Back gate

The important points in this work are shown in Figure 2. Many amounts of not only water and oxygen in the air but also photo resist residues appearing in the production process adsorb on the CNT surface, as shown in Figure 2(A). These impurities can give electrons to the CNTs and take electrons out of them, resulting in a large time-variation of the electric current and a hysteresis in

voltage-current characteristics of the CNT-FETs. Until now, complete removal of the photoresist residues has not been successful. In this work, the development of a production process for making the CNT

surface water-, oxygen-, and photoresist residue-free is shown. Using this technique, and covering the CNT surface with a protective film, the complete removal of the impurities from the CNT surface has been enabled.



Comparison of Current Stability

Fig. 3

Figure 3 shows the time dependence of the electric current for a CNT-FET produced using a conventional method and a CNT-FET produced using techniques and joint works held by The Institute of Scientific and Industrial Research (Osaka University), the National Institute of Advanced Industrial Science and Technology (AIST), and Japan Science and Technology Agency. The electric current for the conventional CNT-FET exhibits a time-variation of 20 %. On the other hand, the new CNT-FET produced shows almost no time variation in the electric current. The calculated variation is 0.01%, indicating that the operational stability of this new CNT-FET is 1000 times or more than that of the conventional CNT-FET.

Comparison of Hysteresis

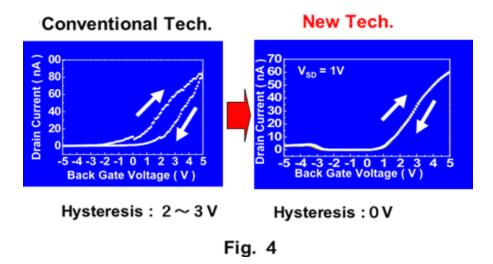


Figure 4 shows the voltage dependence of the electric current for both CNT-FETs. For the conventional CNT-FET, when the applied voltage is increased from -5 to +5 volts, and then decreased from +5 to -5 volts, the voltage-current curve exhibits a hysteresis characteristic of 2-3 volts, while the new CNT-FET exhibits no hysteresis in the current-voltage characteristic.

In this way, the task of removal of time- and voltage-instability of the CNT-FET has been successfully accomplished using this latest technique.

Nanotubes as Sensors

SWNTs may be used as miniaturised chemical sensors. On exposure to environments, which contain Nitrogen Dioxide, Ammonia or Oxygen(in molecular form), the electrical resistance changes. Long metallic carbon nanotubes can be used to create a bio/chemical sensor in one segment while the rest of the nanotube can act as a conductor to transmit the signal.

Composite Materials

Because of the stiffness of carbon nanotubes, they are ideal candidates for structural applications. For example, they may be used as reinforcements in high strength, low weight, and high performance composites. Nanotubes also sustain large strains in tension without showing signs of fracture. In other directions, nanotubes are highly flexible. One of the most important applications of nanotubes based on their properties will be as reinforcements in composite materials. However, there have not been many successful experiments that show that nanotubes are better fillers than the traditionally used carbon fibres.

A main advantage of using nanotubes for structural polymer composites is that nanotube reinforcements will increase the toughness of the composites by absorbing energy during their highly flexible elastic behaviour. Other advantages are the low density of the nanotubes, an increased electrical conduction and better performance during compressive load.

Templates

Because of the small channels, strong capillary forces exist in nanotubes. These forces are strong enough to hold gases and fluids in nanotubes. In this way, it may be possible to fill the cavities of the nanotubes to create nanowires. The critical issue here is the wetting characteristic of nanotubes. Because of their smaller pore sizes, filling of SWNTs is more difficult than filling of MWNTs.

If it becomes possible to keep fluids inside nanotubes, it could also be possible to perform chemical reactions inside their cavities. Especially organic solvents wet nanotubes easily. In this case we could speak of a nanoreactor.

One of the problems in these cases is that nanotubes are normally closed. For the latter applications we have to open the nanotubes. This is possible through a simple chemical reaction: oxidation. The pentagons in the end cap of the nanotubes are more reactive than the sidewall. So, during oxidation, the caps are easily removed while the sidewall stays intact.

CNTs used for cheaper Desalination

Cheap Drinking Water from the Oceans. Carbon nanotube-based membranes will dramatically cut the cost of desalination. A water desalination system using carbon nanotube-based membranes could significantly reduce the cost of purifying water from the ocean. The technology could potentially provide a solution to water shortages worldwide wherever a lack of clean water is a major cause of disease. The new carbon-nanotube based membranes, developed by researchers at Lawrence Livermore National Laboratory (LLNL), are expected to reduce the cost of desalination by 75 percent, compared to reverse osmosis methods used today.

Other Uses

Single-wall carbon nanotubes have a number of revolutionary uses, including being spun into fibers or yarns that are more than 10 times stronger than any current structural material. In addition to uses in lightweight, high-strength applications, these new long metallic nanotubes also will enable new types of nanoscale electro-mechanical systems such as micro-electric motors, nanoscale diodes, and nanoconducting cable for wiring micro-electronic devices. Because of the great mechanical properties of the carbon nanotubule, a variety of structures has been proposed ranging from everyday items like clothes and sports gear to combat jackets and space elevators (The Space Elevator, by Brad C. Edwards, NASA). However, the space elevator will require further efforts in refining carbon nanotube technology, as the practical tensile strength of carbon nanotubes can still be greatly improved. Other uses include applications in nanoscale electronics, where the nanotubes can be used as conducting or insulating materials.

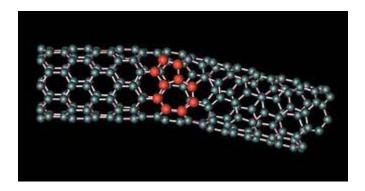


Fig: The joining of two carbon nanotubes with different electrical properties to form a diode has been proposed.

For example, joining together two nanoscale carbon tubes with differing electronic properties could create nanoscale diodes. Even more promising are uses that take advantage of the astonishing strength of the tubes, such as in the creation of super strong carbon nanotube yarns.

For perspective, outstanding breakthroughs have already been made. Single and multi-walled nanotubes can produce materials with toughness un-matched in the man-made and natural worlds.

Drawbacks of Carbon-nanotubes

Nanotube cost, polydispersity in nanotube type, and limitations in processing and assembly methods are important barriers for some applications of single-walled nanotubes.

Problems like purification, separation of carbon nanotubes, control over nanotube length, chirality and desired alignment, low thermal budget as well as high contact resistance are yet to be fully resolved. The main problem with C-nanotubes when used as reinforcements in composite materials is to create a good interface between nanotubes and the polymer matrix, as nanotubes are very smooth and have a small diameter which is nearly the same as that of a polymer chain. However, there have not been many successful experiments that show that nanotubes are better fillers than the traditionally used carbon fibres.

Nanotube aggregates, which are very common, behave different to loads than individual nanotubes do. Limiting factors for good load transfer could be sliding of cylinders in MWNTs and shearing of tubes in SWNT ropes. To solve this problem the aggregates need to be broken up and dispersed or cross-linked to prevent slippage.

Carbon nanotubes are quite popular now for their prospective electrical, thermal, and even selective-chemistry applications. Accordingly, their use will be limited until large quantities of these nanomaterials can be produced that are monodisperse in their structure and properties.

However, many technological hurdles need to be overcome before large-scale applications reach the marketplace. For example, the techniques that are used to build electronic components from nanotubes are painstaking and utterly inappropriate for mass production. But perhaps the most severe limitation is that high-quality nanotubes can only be produced in very limited quantities commercial nanotube soot costs 10 times as much as gold!

Conclusion

Nanotubes appear destined to open up a host of new practical applications and help improve our understanding of basic physics at the nanometre scale.

Nanotechnology is predicted to spark a series of industrial revolutions in the next two decades that will transform our lives to a far greater extent than silicon microelectronics did in the 20th century. Carbon nanotubes could play a pivotal role in this upcoming revolution if their remarkable structural, electrical and mechanical properties can be exploited.

The remarkable properties of carbon nanotubes may allow them to play a crucial role in the relentless drive towards miniaturization at the nanometre scale.

Lack of commercially feasible synthesis and purification methods is the main reason that carbon nanotubes are still not widely used nowadays. At the moment, nanotubes are too expensive and cannot be produced selectively. Some of the already known and upcoming techniques look promising for economically feasible production of purified carbon nanotubes.

Some future applications of carbon nanotubes look very promising. All we need are better production techniques for large amounts of purified nanotubes that have to be found in the near future. Nanotubes promises to open up a way to new applications that might be cheaper, lower in weight and have a better efficiency.

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