

## UNDERSTANDING NANOMATERIALS

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*(Continued from previous issue)*

### QUANTUM LASERS

Semiconductor lasers are key components in a host of widely used technological products, including compact disc players and laser printers, and they will play critical roles in optical communication schemes. The basis of laser operation depends on the creation of nonequilibrium populations of electrons and holes, and coupling of electrons and holes to an optical field, which will stimulate radiative emission. Calculations carried out in the early 1970s predicted the advantages of using quantum wells as the active layer in such lasers: the carrier confinement and nature of the electronic devices operating at lower threshold currents than lasers with “bulk” active layers. In addition, the use of a quantum well, with discrete transition energy levels dependent on the quantum well dimensions (thickness), provides a means of “tuning” the resulting wavelength of the material. The critical feature-size-in this case the thickness of the quantum well—depends on the desired spacing between energy levels. For energy levels of greater than a few tens of millielectron volts (meV, to be compared with room temperature thermal energy of 25 meV), the critical dimension is approximately a few hundred angstroms.

Even greater benefits have been predicted for lasers with quantum dot active layers. It was

predicted in the early 1980s that quantum dot lasers should exhibit performance that is less temperature-dependent than existing semiconductor lasers, and that will in particular not degrade at elevated temperatures. Other benefits of quantum dot active layers include further reduction in threshold currents and an increase in differential gain—that is, more efficient laser operation. Stimulated recombination of electron-hole pair takes place in the GaAs quantum well region, where the confinement of carriers and of the optical mode enhances the interaction between carriers and radiation. The population inversion necessary for lasing occurs more efficiently as the active layer material is scaled down from bulk (3-dimensional) to quantum dots (0-dimensional). However, the advantages in operation depend not only on the absolute size of the nanostructure in the active region, but also on the uniformity of size. A broad distribution of sizes “smears” the density of states, producing behavior similar to that of bulk material. Figure 10 shows a comparison amongst typical laser gains that are obtained from various typical laser gains that are obtained from various quantum structures (wells, wires and dots) prepared from the same semiconductor materials. As it is evident, quantum dot laser is of the highest quality as far as the gain and energy tunability is concerned.

Although the self-assembled dots have provided an enormous stimulus to work in this

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field, there remains a number of critical issues involving their growth and formation : greater uniformity of size, controllable achievement of higher quantum dot density, and closer dot-to-dot interaction range will further improve laser performance.

### **CARBON NANOTUBES—A MAJOR BREAKTHROUGH IN TRANSISTOR TECHNOLOGY**

The features of conventional microelectronic circuits are getting smaller and smaller and will soon reach the limit imposed by the fundamental properties of silicon. Physicists are optimistic that *carbon nanotubes* can step into the breach because of their remarkable electronic and mechanical properties. These nanotubes are tiny cylinders of carbon atoms that measure atoms 10 atoms across, are 500 times smaller than today's silicon-based transistors and 1000 times stronger than steel. Interest from the research community first focused on their exotic electronic properties, since nanotubes can be considered as prototypes for a one-dimensional quantum wire. In 1998, it was demonstrated for the first time that such a carbon nanotube can be used as a transistor. The IBM scientists in 2001 made a breakthrough in transistor technology by building world's first array of transistors out of carbon nanotubes. This achievement was an important step in finding materials that can be used to build computer chips when silicon-based chips cannot be made. That achievement was indeed a major step towards building molecular scale electronic devices. The big question, however, is : will the performance of these molecular transistors be really be able to supersede that of the conventional silicon

devices? Certainly if the nanotube transistor has to succeed, it will need a molecular circuitry that beats the microchips in size and speed. In a distant future, such molecular nanochip devices may become the standard in electronics.

Basically, an ideal carbon nanotubes can be thought of as a hexagonal network of carbon atoms that has been rolled up to make a seamless cylinder. Just a nanometre across, the cylinder can be tens of microns long and each end is "capped" with a half a fullerene molecule. Let us now discuss what fullerene is. One of the major breakthroughs that chemistry witnessed over the past few decades was the following realization that pure carbon can occur not only in the forms of three-dimensional lattice of diamond (where each carbon atom has four neighbours) and the layer-cake structure of graphite (where each layer is tilted with hexagons), but also in a variety of molecular or cluster-like forms that can be described as graphite layers rolled up to balls or cylinders. The most symmetrical species is  $C_{60}$  and has the shape of a soccer ball. These large carbon-cage molecules are called "buckminsterfullerenes" or simply as "buckyballs". Figure 11 shows a diagram of a fullerene structure where each of the 60 corners is surrounded by two hexagons and 1 pentagon.

The first indication of  $C_{60}$  came from an observation of a prominent peak in mass spectra of soot particles obtained by vaporizing graphite and condensing the carbon vapour, although the species was not recognized as a well-defined molecule. Later in 1985, during a collaborative research of Hary Kroto and Richard Smalley on carbon clusters,  $C_{60}$  emerged as a substantial

peak in mass spectra, and the soccer-ball structure was put forward as a hypothesis. After Wolfgang Kratschmer and Doland Huffman at the Max Planck Institute for Nuclear Physics in Heidelberg, Germany had described a recipe suitable for the bulk synthesis of these soccer ball-shaped molecules, an epidemic spread on fullerene research started.

Fullerenes are fascinating for the scientists as this new allotrope of carbon shows unusual properties. Chemically, they are quite stable; breaking the balls requires temperatures of over 1000°C. At much lower temperatures (a few hundred degrees C) fullerenes “sublime”, that means the balls don't break; they just separate from the solid intact. This property is used in growing crystals and thin films of fullerenes. There are other peculiar properties of these new carbon materials. Since  $C_{60}$  is highly electronegative, it readily forms compounds with electropositive elements, such as alkali metals. Indeed, such studies yielded a new set of fascinating materials. For example, adding 3 alkali atoms to a  $C_{60}$  molecule results in a material that goes superconducting at quite high temperatures (10-40 K).

Historically, carbon nanotubes appeared as a byproduct of the phenomenon, known as “fullerene chemistry”. In 1991, Sumio Iijima<sup>11</sup> of the NEC research laboratory in Tsukuba, Japan, while trying to optimize his procedures to produce fullerenes, slightly changed the experimental parameters in his discharge apparatus and was surprised to see that instead of soccer balls he obtained long and thin fibrils. Electron microscopy revealed these fibres to consist of concentrically stacked graphite

cylinders, whose ends were capped with fullerene-like hemispheres. Figure 12 shows schematic representations of a carbon nonotube made up of a rolled-up graphite sheet.

Theoreticians predicted that individual tubes made up of rolled graphite should have intriguing properties. Ordinary graphite is a conductor in the directions parallel to its carbon layers, and an insulator in the direction perpendicular to them. Graphite looks like a sheet of chicken wire, a tessellation of hexagonal rings of carbon. Sheets of graphite in our pencil lay stacked on top on one another, but they slide past each other and can be separated easily, which is how it is used for writing. However, when coiled, the carbon arrangement becomes very strong. In fact, nanotubes have been known to be up to one hundred times as strong as steel and almost two millimeters long! These nanotubes have a hemispherical “cap” at each end of the cylinder. They are light, flexible, thermally stable, and are chemically inert. They have the ability to be either metallic or semi-conducting depending on the “twist” of the tube.

Naively, one could assume that rolling up the layers would result in a one-dimensional conductor along the axis of the tube, while the orthogonal direction (the plane cutting the tube at a right angle) has electrons running around in circles, and not getting anywhere. Although there are lots of different ways of a rolling up a graphite layer generating different tubes with a given radius, only two will be symmetrical with respect to rotation around their axis. Based on the appearance that the rim of such tubes takes along orthogonal cuts, they are called *zigzag* and *armchair* tubes. All other kinds of tubes have

screw-like patterns, resulting in a chirality. They are normally characterized by the angle ( $\theta$ ) at which their rolling vector is positioned to the zigzag line. That is, one could make both one-dimensional metal wires and semiconductors from the same material—the same atoms in the same pattern—just by changing this angle. Figure 13 is a schematic representation of the conversion of a graphite layer (honeycomb pattern) into a nanotube, characterized by the wrapping vector<sup>12</sup>.

The so-called chiral vector of the nanotube,  $C_h$ , is defined by  $C_h = n\tilde{a}_1 + m\tilde{a}_2$ , where  $\tilde{a}_1$  and  $\tilde{a}_2$  are unit vectors in the two-dimensional hexagonal lattice, and  $n$  and  $m$  are integers. Theoretical calculations have predicted that because of quantum mechanical effects electronic properties of carbon nanotubes will depend not only on their radius, but also, very sensitively, on the chiral angle  $\theta$  which is the angle between  $C_h$  and  $\tilde{a}_1$ . When the graphite sheet is rolled up to form the cylindrical part of the nanotube, the ends of the chiral vector meet each other. The chiral vector thus forms the circumference of the nanotube's circular cross-section, and different nanotube structures. Armchair nanotubes are formed when  $n = m$  and the chiral angle is  $30^\circ$ . Zigzag nanotubes are formed either  $n$  or  $m$  are zero and the chiral angle is  $0^\circ$ . All other nanotubes, with chiral angles intermediate between  $0^\circ$  and  $30^\circ$ , are known as chiral nanotubes. The diameter and chiral angle, both of which depend on  $n$  and  $m$ , determine the properties of nanotubes. Measurements of the nanotube diameter and the chiral angle have been made with scanning tunneling microscopy and transmission electron microscopy.

The unique electronic properties of carbon nanotubes are due to the quantum confinement of electrons normal to the nanotube axis. Around the circumference of the nanotube, periodic boundary conditions come into play. For example, if a zigzag or armchair nanotube has 10 hexagons around its circumference, the 11th hexagon will coincide with the first. Going around the cylinder once introduces a phase difference of  $2\pi$ . Because of the quantum confinement, electrons can only propagate along the nanotube axis, and so their wave vectors point in this direction. The resulting number of one dimensional conduction and valence bands effectively depends on the standing waves that are set up around the circumference of the nanotube. The density of electronic states as a function of energy has been calculated for a variety of nanotubes. While conventional metals have a smooth density of states, these nanotubes are characterized by a number of singularities, where each peak corresponds to a single quantum subband. Figure 14 shows the calculated "density of states" as a function of energy for a variety of nanotubes<sup>14</sup>.

Intensive research is going on towards the preparation, characterization and modeling of carbon nanotubes. To date, nanotube structures are largely a disordered entanglement of tubes with almost no control of growth site. There are several growth techniques which are based on the deposition of carbon onto a surface either directly (are deposition, laser ablation) or through gas phase decomposition (CVD deposition). Rice University group found an efficient way for the first time to produce bundles of single-wall nanotubes in 1996 based on laser vaporization

of a carbon target in a furnace of 1200°C with uniform vaporization and better control of the growth conditions. A cobalt-nickel catalyst helped the growth of the nanotubes, presumably because it prevented the ends from being “capped” during synthesis, and about 70-90% of the carbon target could be converted to single-wall nanotubes. Research Groups at IBM Zurich demonstrated a radically new method of growing single-wall carbon nanotubes in ordered arrays. The growth was based on combining carbon in the form of C<sub>60</sub> molecules with a nickel catalyst and heating to over 900°C for a few minutes.

### EXCITING PROPERTIES OF CARBON NANOTUBES

The intriguing structures of carbon nanotubes have sparked much excitement in the recent years and a large amount of research has been dedicated to their understanding. Currently, the physical properties are still being discovered and disputed. What makes it so difficult is that nanotubes have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist). To make things more interesting, besides having a single cylindrical wall (SWNTs), nanotubes can have multiple walls (MWNTs)—cylinders inside the other cylinders.

Depending on the size and shape of a carbon nanotube, electronic properties can be of metallic or semiconducting. A key breakthrough came in 1994, when Charles Oik and Joseph Heremans of the General Motors Research Laboratory in Michigan measured the properties of individual multi-wall nanotubes using a STM. These results

provided the first confirmation that some nanotubes are metallic, while others are semiconducting. They showed that the bandgap for semiconducting nanotubes is inversely proportional to diameter of the tube. In 1998, Stephan Frank *et al.* experimented on the conductance of nanotubes<sup>14</sup>. Using a SPM, he carefully contacted nanotube fibers with a mercury surface. His results revealed that the nanotube behaved as a ballistic conductor with quantum behavior. The MWNT conductance jumped by increments of 1 G<sub>0</sub> as additional nanotubes were touched to the mercury surface. The value of G<sub>0</sub> was found to be approximately 1 / 12.9kΩ<sup>-1</sup>, where G<sub>0</sub> = 2e<sup>2</sup> / h.

IBM's Thomas J Watson Research Centre found that van der Waals interaction between nanotubes and surfaces on which they are placed on. Thus the researchers were able to change the nanotubes' positions and orientations, and to alter their shape, by bending them. Using calibrated AFM forces, it is therefore possible to distort the nanotubes which can then be stabilized by the strong interaction with the surface.

The problem the scientists face in using carbon nanotubes as transistors is that all synthetic methods of production yield a mixture of metallic and semiconducting nanotubes which “stick together” to form ropes or bundles. This compromises their usefulness because only semiconducting nanotubes can be used as transistors; and when they are stuck together, the metallic nanotubes overpower the semiconducting nanotubes. Since nanotubes are typically a few microns long, electrical contacts can be made by modern lithographic techniques.

Single-wall carbon nanotubes thus provide a unique system for studying single-molecule transistor effects, in which an electrode close to the conducting nanotube is used to modulate the conductance. Several complementary technical approaches are being made successfully to demonstrate molecular-scale electronic nanomemory arrays. Hewlett-Packard Laboratories has developed a process to fabricate crossbar molecular circuits with the highest density electronically addressable memory reported to date.

Carbon nanotubes exhibit extraordinary mechanical properties. In 1996 a group led by Thomas Ebberson at the NEC Research Institute in Princeton estimated the Young's modulus of carbon nanotube by measuring the vibrations of the free end of a nanotube that was clamped at the other end. Their estimates were consistent with the exceptionally high values of Young's modulus (over 1 Tera Pascal) already measured for a graphene sheet. A carbon nanotube is as stiff as diamond with estimated tensile strength of 200 Giga Pascal. Single-wall carbon nanotubes are also expected to be very strong and to resist fracture under extension. They are, unlike carbon fibres, remarkably flexible. They can be twisted, flattened and bent into small circles or around sharp bends without breaking. All these unique properties are ideal for reinforced composites, nano-electromechanical systems.

### DIVERSE APPLICATIONS

The real burst in the commercialization of nanoparticle production has occurred over the last ten years or so because of its wide range of applications. The diverse range of inorganic

materials that can now be made in nano-sized crystallites or particles includes not only the familiar examples of buckyballs, carbon nanotubes, and cadmium selenide (CdSe) quantum dots, but also a wide range of metals and metal oxides, sulphides, fluorides, carbonates, nitrides, silicates, and several other material classes. Many of these materials can be synthesized in different morphological form<sup>15</sup>, each important for its characteristic feature and applications. The motivation to develop a wide range of nanoparticle chemistries and morphologies stems from the extraordinary range of applications that is gradually unfolding. The significant growth of companies that are offering products in the nanomaterials area seems to be incredible. Their interests are not limited to traditional materials science markets. In the life sciences area, for example, several start-ups are addressing the challenges posed by bioterrorism by developing sensors that use nanoparticles of CdSe QDs that are functionalized with strands of DNA. Others are exploring nanoparticles of iron metal or iron oxide as magnetic delivery systems for drugs.

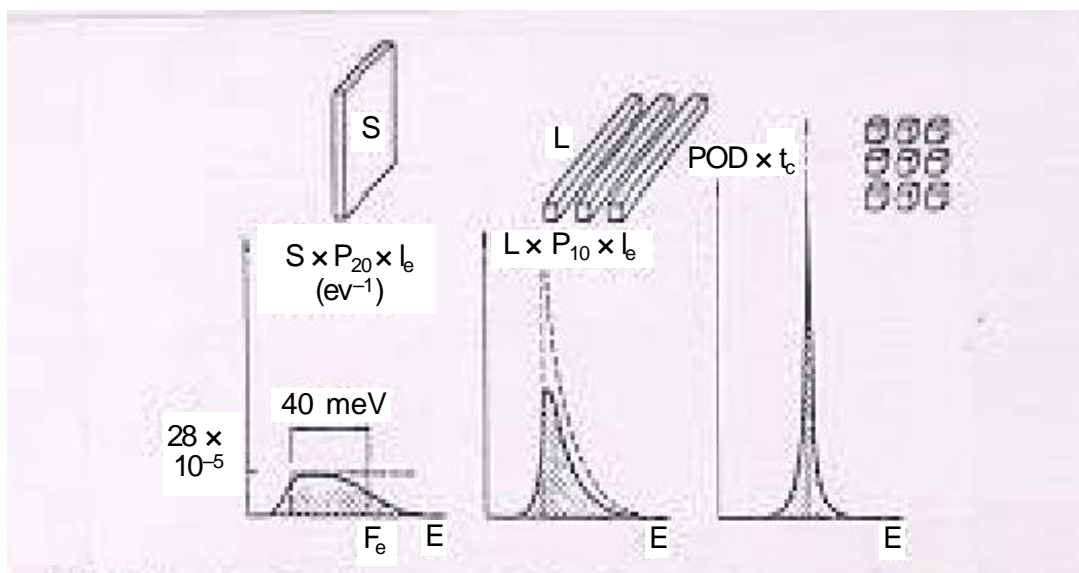
Security devices based on nanomaterials are also very fashionable. Nanophosphors made of rare-earth phosphates are being developed for security printing, and invisible nanorods of Au or Ag can be used as sophisticated bar codes. In the catalysis area, cerium dioxide (CeO<sub>2</sub>) nanocrystals are being used as fuel additives for diesel engines, where they improve fuel efficiency and reduce emissions.

The fields of bio and organic nanoparticles are also mushrooming. Block copolymers can

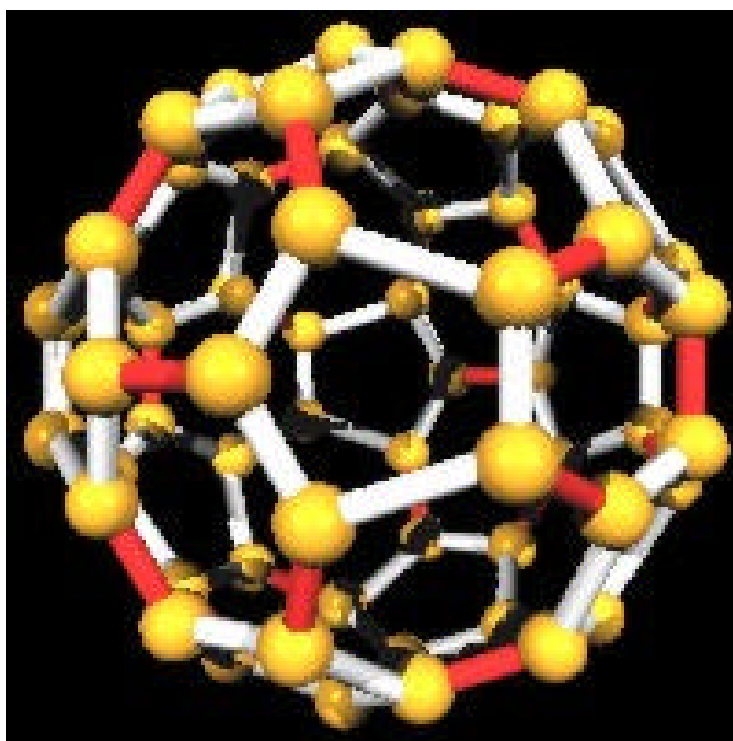
self-assemble to form nanostructures that create excellent nanotemplates for laying down other materials. It is very likely that nanodevices can do potentially more than current drugs and diagnostic tests. However, for the full potential of nanotechnology in medicine to be realized, nanomachines will have to be 'smarter' so that they are capable of recognizing changes caused by the treatment and report back on the results. These tasks require built-in sensors for target recognition and molecular switches to convert the signal to response.

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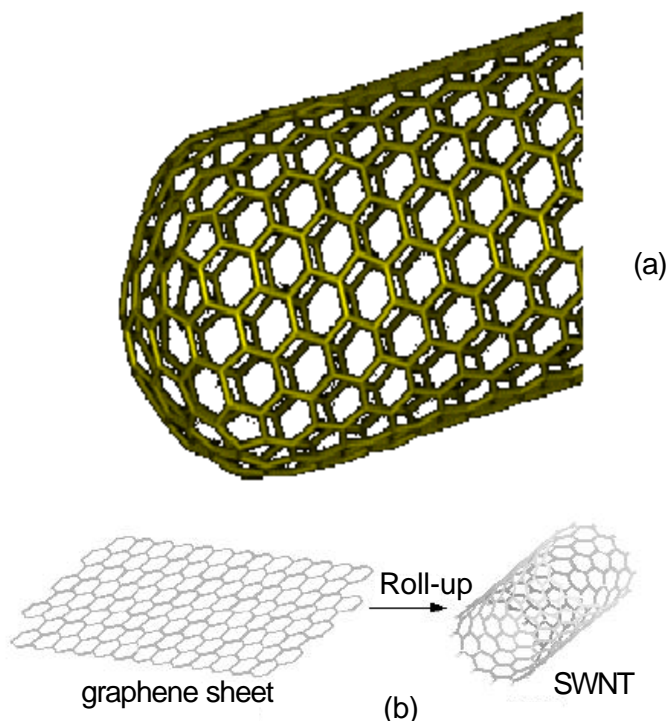
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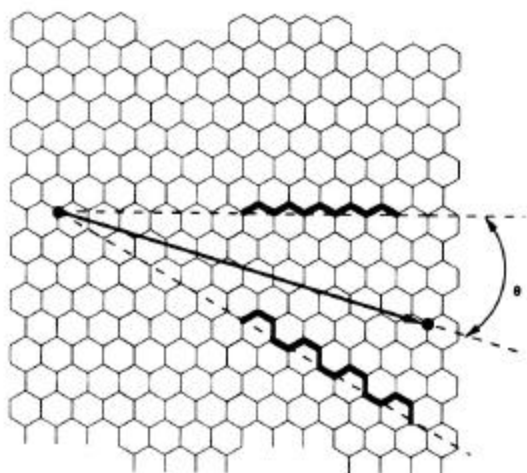
**Fig.10.** Laser gain curves for semiconducting 2D, 1D and 0D structures. Increasingly narrower density of states close to band edge leads to effective narrowing of energy width and hence lower threshold current density.



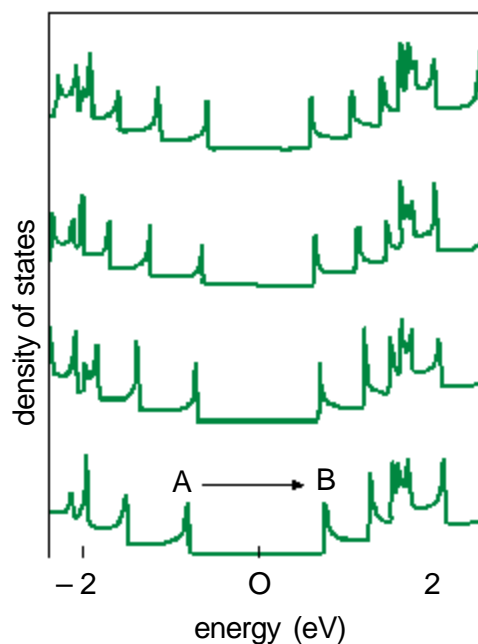
**Fig.11.** Schematic structure of a soccer-ball fullerene ( $C_{60}$ ) molecule. red bonds are double bonds, and white ones are single bonds.



**Fig.12.** (a) Single walled carbon nanotube : a prototype for a one-dimensional quantum wire. (b) Hexagonal network of carbon atoms are rolled up to make a seamless cylinder.



**Fig.13.** The conversion of a graphite layer (honeycomb pattern) into a nanotube can be characterized by the wrapping vector, which can point from one corner to any other analogous one (solid circles). When the sheet is rolled up, the base and the point of this vector will meet and it will form a circle. The wrapping direction shown as a horizontal line is special in that the resulting tubes will be symmetrical with respect to the long axis of the cylinder. Cutting such a tube at a right angle to its axis will result in a "zigzag" edge like the line drawn more thickly.



**Fig.14.** Calculated "density of states" as a function of energy for a variety of nanotubes.