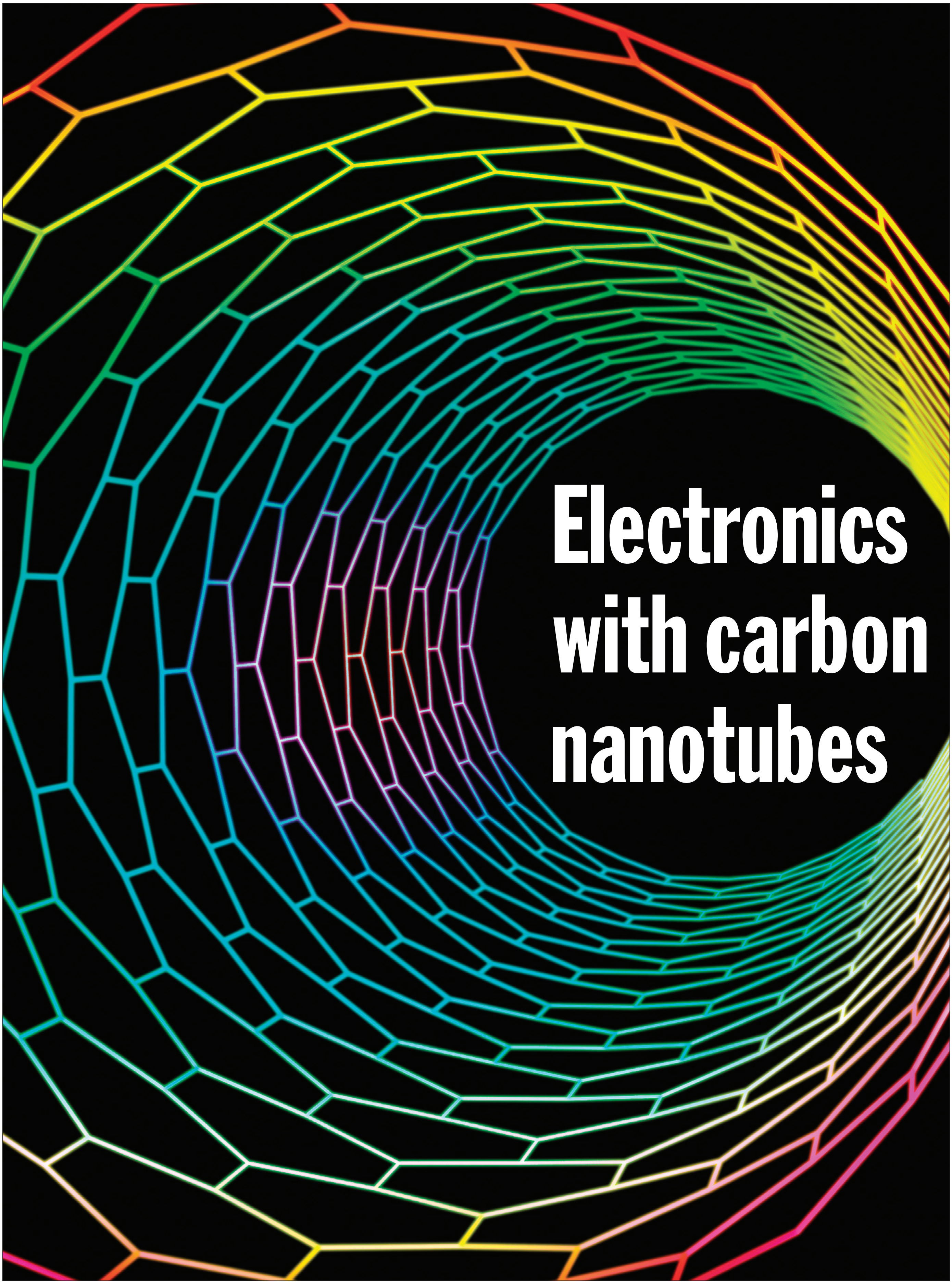

Electronics with carbon nanotubes

Pasieka/Science Photo Library

Once the preserve of pure research, carbon nanotubes are being turned into switches, transistors and light-emitting devices with highly useful properties, as **Phaedon Avouris** explains

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From mobile phones and laptops to Xboxes and iPods, it is difficult to think of any aspect of modern life that has not been touched by developments in electronics, computing and communications over the last few decades. Many of these technological advances have arisen from our ability to create ever smaller electronic devices, in particular silicon-based field effect transistors (FETs), which has led to denser, faster and less power-hungry circuits. The problem is that this device miniaturization, or "scaling", cannot continue forever; fundamental scientific and technological limitations exist that will make it impossible to build better performing silicon devices below a certain size.

This potential show-stopper has inspired a worldwide effort to develop alternative device technologies based on 1D materials or those that exploit the spin, as well as the charge, of electrons. One promising and, in principle, simpler approach is to maintain the operating concept of today's silicon-based FETs but to replace a key component of the device – the semiconducting silicon channel – with 1D nanostructures that have much more versatile electrical-transport properties.

Among the different 1D materials that have been developed, those with the most desirable properties are "single-walled" carbon nanotubes, which were first created in 1993 by Sumio Ijima at the NEC Fundamental Research Laboratory in Tsukuba, Japan, and by Donald Bethune of IBM's Almaden Research Center in California. These materials are hollow tubes made from rolled up sheets of carbon just one atom thick, otherwise known as graphene. Single-walled nanotubes contain just one rolled up sheet, while "multi-walled" nanotubes contain several tubes nested inside one another like Russian dolls.

Several microns, even centimetres, long but with a diameter of just 1–2 nm, carbon nanotubes are almost ideal 1D objects. They are also an engineer's dream, having exceptionally high tensile strength – a Young's modulus 10 times that of steel – and conducing heat very well along their length. But what makes carbon nanotubes of particular interest to the electronics industry are their excellent electrical properties. Depending on the precise arrangement of the carbon atoms, nanotubes can either be metals or semiconductors, with the latter forming the basis of new ultrafast FETs. Moreover, we could one day build electronic circuits in which transistors made from semiconducting nanotubes are linked by "interconnects" made from metallic nanotubes.

Even more exciting is that we can now use carbon nanotubes to generate and detect light. In fact, it is possible to create carbon-nanotube devices that can operate either as a transistor, a light emitter or a light detector simply by changing the supplied voltages. Light sources and detectors built from carbon nanotubes also open the door to single-molecule spectroscopy. Carbon nanotubes could even be used to send light pulses from one microchip to the next and open up the possibility of having both electric and optoelectronic technologies on the same material.

Special behaviour

The remarkable electrical properties of carbon nanotubes stem from the unusual electronic structure of graphene, which is a single layer of carbon atoms arranged in a honeycomb lattice. The difference between graphene and a standard semiconductor material can best be understood by considering the individual energy levels of the charge carriers (electrons or holes), which are spread out into a series of bands. For an n-type semiconductor, the material can semiconduct if electrons are excited from the highest energy occupied band (the "valence" band) into the lowest unfilled band (the "conduction" band). The gap between the valence and conduction bands is known as the band gap.

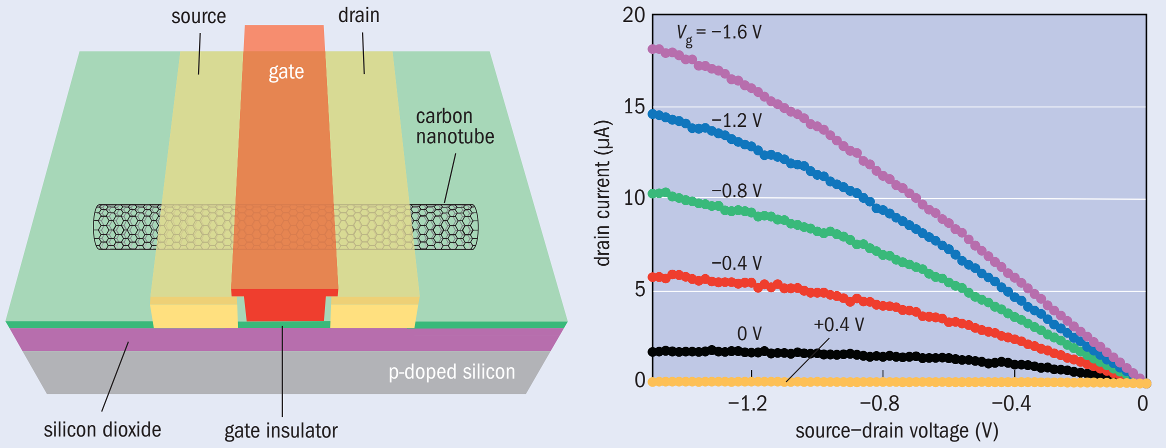
The honeycomb structure of graphene, however, causes its conduction and valence bands to touch at six separate points at the energy of the highest occupied electronic state at zero temperature (the Fermi energy). Strange things therefore happen when a graphene sheet is rolled up to form a carbon nanotube. Electrons are restricted in how they can move around the circumference of the tube because the component of momentum around the circumference, k_ζ, is quantized and equal to $2\pi n/C$, where n is a non-zero integer and C is the circumference. On the other hand, electrons can move freely along the length of the tube and the component of momentum in that direction is a continuous variable. The quantization of k_ζ, however, leads to a discrete set of energy sub-bands for each tube, which, depending on their relationship with graphene's band structure, leads to the tube either being a metal or a semiconductor.

Like any macroscopic structure, a nanotube has a certain resistance, capacitance and inductance, which arise from the structure of the nanotube and how it interacts with other objects. These properties are important because they determine the performance of any devices made from the nanotube. The total resistance of a nanotube is relatively low because the electrons in it scatter very little from defects and lattice vibrations – the usual source of resistance in bulk materials. However, carbon nanotubes also have an additional, quantized resistance arising from contacts between the tube and any macroscopic metallic electrodes to which it is attached. There are also other forms of contact resistance, for example due to the presence of "Schottky barriers" at the interface be-

At a Glance: Nanotube electronics

- First created in the early 1990s, carbon nanotubes are tiny cylinders made from rolled up sheets of graphene – the material found in the graphite in pencil lead
- These tiny 1D tubes are very strong but also have excellent electronic properties, which allows them to be used used to make ultrafast field effect transistors
- Researchers have recently been able to make carbon-nanotube transistors in which either electrons or holes flow – or even both
- Carbon nanotubes in which just one type of charge carrier flows can function as ultrabright light-emitting diodes
- Nanotubes can also operate as primitive solar cells by converting light into electron–hole pairs

1 Nanotubes as transistors

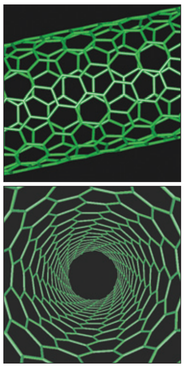


Field effect transistors (FETs) consist of a semiconducting channel connected at either end to "source" and "drain" electrodes and separated from a third, "gate", electrode by a thin dielectric film called the gate insulator. In a carbon-nanotube FET, however, the silicon channel is replaced by one or more semiconducting nanotubes (left). Applying a voltage to the gate, V_g, raises or lowers the energy barrier for the carriers in the nanotube. In the case of a p-type nanotoube, a sufficiently positive value of V_g will raise the barrier so high that no electrons can flow from the source to drain and so turn the transistor "off". A negative V_g above a certain threshold, however, will lower the barrier and turn the transistor "on". Shown here is the drain current as the source–drain voltage is changed for various values of V_g.

tween metallic electrodes and semiconducting nanotubes or parasitic resistance due to bad contacts.

One important and unique property of carbon nanotubes is that if there is no scattering inside the tube, the electrons flow "balistically". In other words, they move without losing any energy in the process. The distance over which a nanotube can conduct in this way depends on various factors, such as temperature, structural perfection and the size of the driving electric field. Under typical operating conditions, ballistic transport can be achieved over lengths of 100 nm, which is perfect for modern electronic devices. As a nanotube becomes longer or the applied field is increased, the electrons start to scatter more and more until eventually – above a certain length – the nanotubes start behaving like ordinary materials. Nevertheless, the electrons in these long tubes are still more than 100 times more mobile than in bulk silicon, which is great news in the search for faster electronic devices.

As an isolated object, a carbon nanotube has a quantum capacitance, C_Q, of roughly $10^{-16}\,\mathrm{F}\,\mu\mathrm{m}^{-1}$, with the exact figure depending on the energy distribution of its electronic states. But if a nanotube is incorporated into a FET, there is an additional electrostatic capacitance that arises from the tube's coupling to surrounding conductors and this is roughly equal to the capacitance of the transistor's " gate" electrode, C_G. As the two capacitances are in series, the total, C_T, is given by $1/C_T = 1/C_G + 1/C_Q$. Usually, C_G dominates the total capacitance of the device because it is about 10 times smaller than C_Q. However, if one tries to make a carbon-nanotube FET smaller or to use a gate with a higher dielectric constant, the gate capacitance starts to increase. Eventually it can exceed C_Q, which can then dominate the total capacitance. At this point one reaches the ultimate scaling limit of the device because C_Q is now controlled by the quantum nature of the nanotube, rather than the structure of the device itself.



Tiny but shiny
Carbon nanotubes can be made to emit light when incorporated in a transistor.

Nanotubes as electrical switches

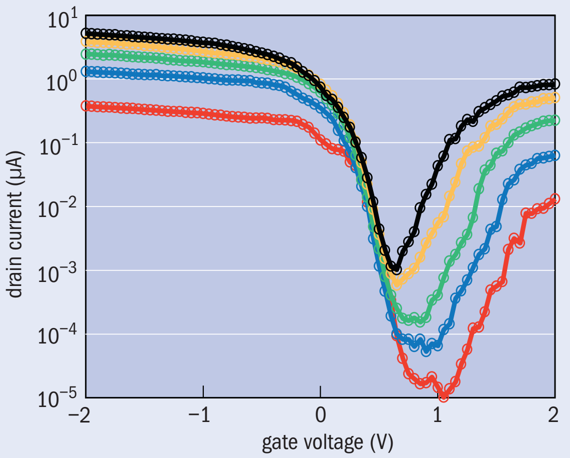
The main appeal of semiconducting carbon nanotubes is that they can be switched on and off, which means that they can be used as a new material for transistors. Conventional FETs have of course been around since the early 1960s and are usually made from a piece of semiconductor, known as the channel, that is connected at opposite ends to two metallic electrodes called the source and the drain. The channel is separated from the gate electrode by a thin dielectric film called the gate insulator, usually silicon dioxide.

Applying a voltage to the gate raises or lowers the energy barrier for the carriers in the semiconductor depending on the polarity of the voltage. In the case of a p-type semiconductor, in which the charge carriers are holes, a sufficiently positive gate voltage will raise the barrier in the valence band so high that no holes can flow, i.e. the transistor is turned "off". A negative gate voltage above a certain threshold, however, will lower the barrier and turn the transistor "on". (The reverse is the case for electrons travelling through the conduction band of an n-type semiconductor.)

The first carbon-nanotube FETs were created in 1998 by researchers at Delft Institute of Technology in the Netherlands, IBM Research in Yorktown and later Stanford University. These devices behave in very similar ways to conventional FETs except that the silicon channel is replaced by one or more semiconducting nanotubes (figure 1). However, nanotubes have several unique advantages as a channel material. The most important is that they conduct balistically, which could lead to faster devices. Second, there is good "coupling" between the electric field of the gate and the channel, which means that one can make the devices shorter without losing the ability to control the current in the channel via the gate voltage – a common problem in conventional FETs.

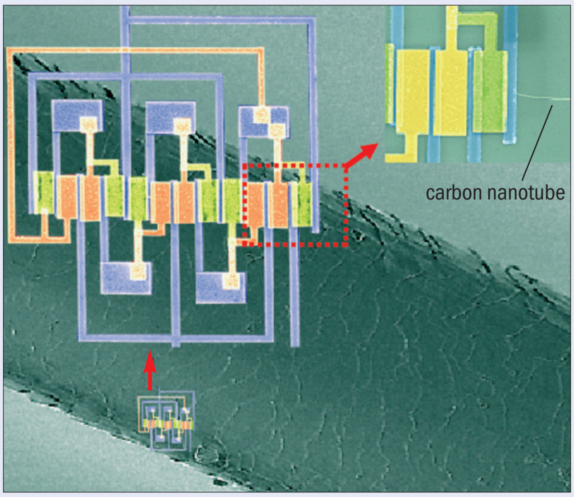
Carbon nanotubes also have smooth surfaces, so there is no scattering from irregularities that would

2 Ambipolar transistors



Carbon-nanotube transistors can conduct both types of charge carrier: holes can travel through them if the gate voltage is highly negative, whereas electrons conduct if the voltage is positive. At intermediary voltages, however, both electrons and holes flow and the two currents are equal when the gate voltage is half of that between the source and drain. The drain current is shown here for an increasingly negative source–drain voltage from red to black. Such transistors are useful because they can emit light when the electrons and holes recombine.

3 From research to reality



This electron micrograph, obtained by researchers at IBM, shows the most complex circuit ever built from a single molecule. It is of a "five-stage ring oscillator" based on a single carbon nanotube. The circuit (bottom left) has been superimposed on a human hair to show its relative size. The main image is an enlarged version of the circuit, while the nanotube itself can be seen in the further enlargement of one portion of the circuit (top right).

otherwise reduce the mobility of the charge carriers. Moreover, all the carbon atoms on the surface of the material are bonded to one another, which means that there are no "dangling" bonds that trap unwanted charge. This means that gate insulators other than silicon dioxide, which is normally used in conventional transistors to get rid of dangling silicon bonds in the channel, can therefore be used. Indeed, there is a major effort in the electronics industry to move away from silicon dioxide to insulators with higher dielectric constants, as was illustrated in January by announcements from IBM and Intel that they had built a new generation of conventional FETs that use hafnium insulators.

Transistor action

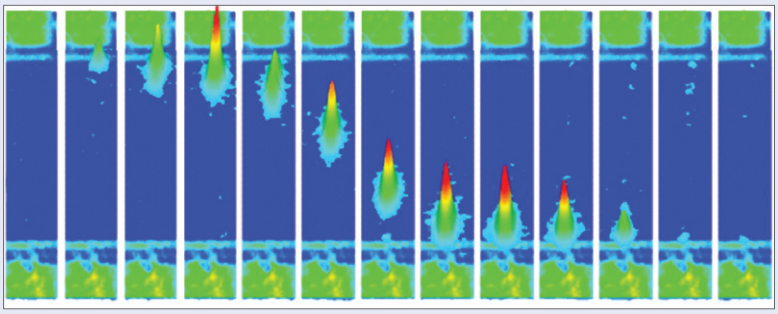
One interesting property of carbon-nanotube FETs is that they are naturally "ambipolar", which means that both electrons and holes can be injected into the channel at the same time. Conventional transistors, in contrast, are "unipolar" because they transport only one type of carrier – either electrons or holes. This is because the metal contacts in carbon-nanotube FETs between the channel and both the source and drain electrodes, which are usually made from palladium, gold, titanium or aluminium, have a different "work function" from the nanotube. Charge therefore moves across the interface until the two Fermi levels become equal. This creates an electric dipole that opposes further charge transfer and forms a Schottky barrier.

There are two such barriers in a carbon-nanotube transistor – one at the source and one at the drain. Depending on the relative size of the barriers for different charge carriers, a FET can sometimes act as a unipolar device and transport only one type of carrier. For example, palladium has a high work function, which means that the valence band of the carbon nanotube lies close to the metal's Fermi level. The barrier across the source contact is then low, allowing holes to flow almost freely across the contact. Electrons trying to enter the channel across the other contact, however, will meet a much higher barrier that can be as large as the gap between the top of the valence band and the bottom of the conduction band. In contrast, if the contacts are made from a metal with a low work function, such as aluminium, the conduction band of the nanotube now lies close to the metal's Fermi level, thereby allowing electrons, but not holes, to flow.

In reality, life is more complex because carrier transport across the metal–nanotube interface is dominated by quantum-mechanical tunnelling through the Schottky barrier, rather than being thermally activated. In other words, the thickness – not just the height – of the barrier is also important. If the two barriers are thin enough, both electrons *and* holes can be injected into the channel. In these ambipolar transistors, holes are injected if the gate voltage is highly negative, while electrons are injected if the voltage is positive (figure 2). When the gate voltage is such that the current is near its minimum, both electrons and holes contribute to the current. When the gate voltage is exactly half that between the source and drain, the electron and hole currents are equal.

Researchers at IBM and elsewhere have been able to fabricate not just single carbon-nanotube devices but also simple circuits such as logic gates

4 Let there be light



Ambipolar carbon-nanotube transistors can emit light when electrons (travelling from the top in this figure) recombine with holes (from below). The advantage of this type of device over, say, light-emitting diodes is that the origin of the light can be moved simply by changing the gate voltage. Carbon nanotubes could therefore be used as ultrasmall adjustable light sources.

Carbon-nanotube FETs, particularly those with large diameter tubes or thin gate oxides, are naturally ambipolar. However, ambipolar devices of this kind are obviously not useful if we want to use such transistors to carry out logic operations because we cannot turn them completely on or off. All we can do with such devices is change the type of carrier flowing through them. Fortunately, as the author and colleagues showed in 2005, there are two possible ways to eliminate ambipolar behaviour and obtain clear switching. One is to use a "double-gated" carbon nanotube: one gate selectively thins the Schottky barriers while another "central" gate switches the bulk of the device. The other is a chemical approach, in which the contact regions of the transistor are doped with electron-donating or electron-accepting molecules that are chemically absorbed onto the surface of the tube. By doping only the contact regions of the tube and using a central gate for switching, the transistor becomes unipolar and we can achieve bulk-like behaviour.

In terms of actual devices, researchers at IBM and elsewhere have so far been able to fabricate not just single carbon-nanotube FET devices but also simple circuits like logic gates. Moreover, my team at IBM has built more complex structures such as "ring oscillators", which contain odd numbers of pairs of n- and p-type transistors and are essential for testing the switching performance of new materials (figure 3). These structures are an ideal model for showing how we can integrate a number of carbon-nanotube devices to achieve specific function, and show that they are compatible with conventional complementary metal-oxide silicon (CMOS) circuit architecture. However, fluctuations in the number and position of the dopants can have a profound effect on device performance, and controlling doping in nano-scale devices is a problem with nanotube FETs. We have shown recently, however, that the ambipolar behaviour of a single, undoped carbon nanotube can be modified and used to implement the CMOS architecture by using gates made from metals with different work functions.

Carbon nanotubes are an ideal system for studying electrical and optical phenomena on the nano scale

Lighting up

One of the most exciting developments in carbon-nanotube research is the recent discovery that nanotubes can emit light. That finding opens the door to circuits in which standard copper interconnects are replaced by optical waveguides made from nanotubes – allowing the possibility of fully integrated optoelectronic circuits.

It is well known that electrons and holes can recombine in a semiconductor to release either heat (in the form of phonons) or light (in the form of photons). This process of "radiative recombination" leads to electroluminescence, which is the basis of solid-state light sources such as light-emitting diodes (LEDs). The key to increasing the intensity of light from a practical LED, however, is to generate and bring together as many electrons and holes as possible. Conventionally, this is achieved at the junction between a p-doped and an n-doped semiconductor. But the interesting feature of ambipolar carbon-nanotube transistors is that we can inject both electrons and holes from the source and drain into the channel at the same time. The 1D character of the nanotube confines the two types of carriers and drives them towards each other – offering the possibility of more intense light emission.

In 2003 James Misewich and co-workers at IBM observed radiative recombination in an ambipolar carbon-nanotube FET for the first time. While the emission mechanism is similar to that of an LED, there is one important difference: the carbon nanotube is not doped, which makes it much easier to fabricate. Best of all, because there is no p–n junction, the light does not originate from a fixed point along the nanotube. Instead, its origin can be moved simply by changing the gate voltage. In other words, carbon nanotubes could be used as an ultrasmall light source that can be adjusted at the micron scale (figure 4).

Localized electroluminescence has also been observed by my team at IBM from particular spots on a single-walled nanotube even when it is operating as a unipolar device. Since light can only be generated when both electrons and holes are present, we can only conclude that electrons and holes are somehow being generated at these spots. Our studies have shown that these light-generating spots include a variety of defects in the gate insulator and at interfaces between materials with different dielectric constants, which seem to produce voltage drops along the nanotube that generate large, local electric fields. These fields can accelerate an electron to such a high energy that it can then lose some of this energy by falling to a lower-energy conduction-band state and emitting an electron–hole pair.

This "impact excitation" mechanism is particularly strong in carbon nanotubes and is interesting for several reasons. For example, unipolar light sources have been found to be brighter and more intense than ambipolar devices because the currents in the former are much higher. Moreover, it is possible to set up a chain reaction in which electrons and holes generated through the excitation mechanism are accelerated by the large electric field, in turn generating further electrons and holes to produce greater light emission.

At IBM we have recently shown how the impact excitation may be implemented in a light-emitting device. We modified a carbon-nanotube FET by cutting a trench in the channel so that there is no gate dielectric between the nanotube channel and the gate. The voltage along the channel therefore plunges suddenly at a specific point (figure 5). Electrons accelerated at the dielectric discontinuity can acquire enough energy to exceed the impact-excitation threshold and generate a bright light with a yield that is about 1000 times greater than that produced by simple recombination in an ambipolar carbon-nanotube FET. Light from a bright nano-scale source of this type could, if properly confined, be used for inter-chip communication, single-molecule spectroscopy and other applications.

Such localized-electroluminescence devices could also be used as an analytical tool to identify defects in either the nanotube itself or in the gate insulator. Currently it is not easy to spot such defects for nanotubes incorporated into a device because transmission electron microscopy or scanning tunnelling microscopy cannot be used.

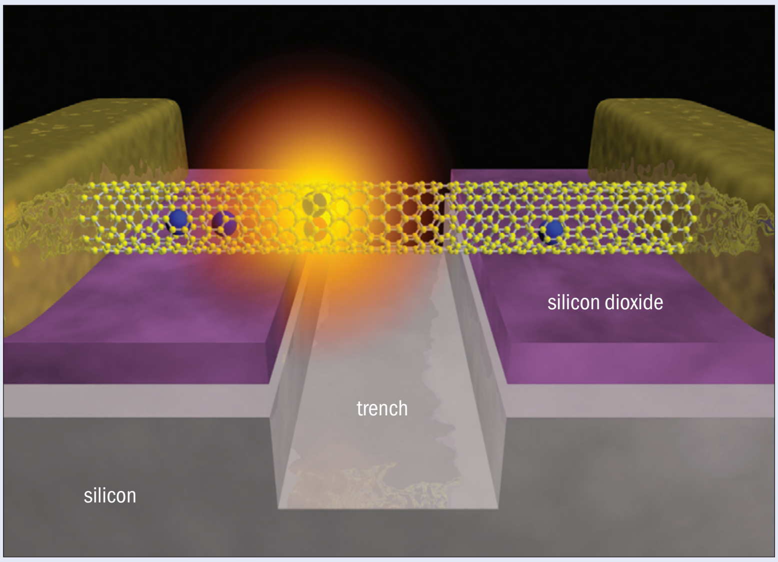
Finally, carbon nanotubes can even operate as photoconductors, in which light can generate free electrons and holes. The current generated by the tube under resonant excitation implies that such devices could be used as nano-sized photodetectors, photoswitches or spectroscopic tools. Alternatively, shining light on a nanotube FET would generate a photo voltage and make it operate as a solar cell. We could further enhance the sunlight-harvesting ability of the device by "decorating" the nanotube with quantum dots or appropriate polymers. In other words, the same carbon-nanotube FET could be used either as a transistor, a light detector, a light emitter or a voltage source. All you need to do to switch between these different modes of operation is to change the electrical input.

The future lies in tubes

In addition to their uses as switches, light emitters and detectors, nanotubes have other applications too. For instance, biosensors can be made from carbon-nanotube transistors by adding chemical groups to the tubes that bind to certain specific biological molecules. When the biomolecule attaches itself to the tube, it changes the electric field produced by the gate and hence alters the current flowing through the device; measuring that change will reveal the presence of the molecule.

So how soon can we expect these developments to occur? The main bottleneck to the development of nanotube electronics and photonics is the material itself. Like many other nanomaterials, nanotubes come in many sizes and structures. The problem is that currently we have no reliable way of mass-producing a single type of carbon nanotube. Although such techniques may eventually be developed, groups at Northwestern University and DuPont, for example, have already reported the isolation of a single type of nanotube from mixtures. Meanwhile, it is even proving possible to take a solution of nanotubes that can "self-assemble" in a controlled way on a wafer to form a pattern that can be directly turned into electronic circuits.

5 Ultrabright light sources



Light can be emitted from unipolar carbon-nanotube FETs even though they only conduct either electrons or holes but not both. This can be achieved by cutting a trench in the channel so that there is no gate dielectric between the nanotube and the gate. The voltage along the channel drops suddenly at this discontinuity, creating large, local electric fields that can accelerate an electron to high energy. The electron then drops to a lower energy and emits an electron–hole pair in the process. The yield of the light emitted when this pair recombines can be about 1000 times greater than that produced by simple recombination in an ambipolar carbon-nanotube FET.

Carbon nanotubes also provide us with an ideal system for studying electrical and optical phenomena on the nanometre scale. These 1D materials with their exotic properties – long the realm of theoretical studies – are now open to experimentation. Nanotube research is also teaching us how to handle and process nanomaterials, helping to develop nanotechnology in general. Through the study of nanotubes, there is no doubt we will continue in the future to obtain novel information on the physics of the nano scale. ■

More about: Nanotube electronics

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