

They are stronger than steel, but the most important uses for these threadlike macromolecules may be in faster, more efficient and more durable electronic devices

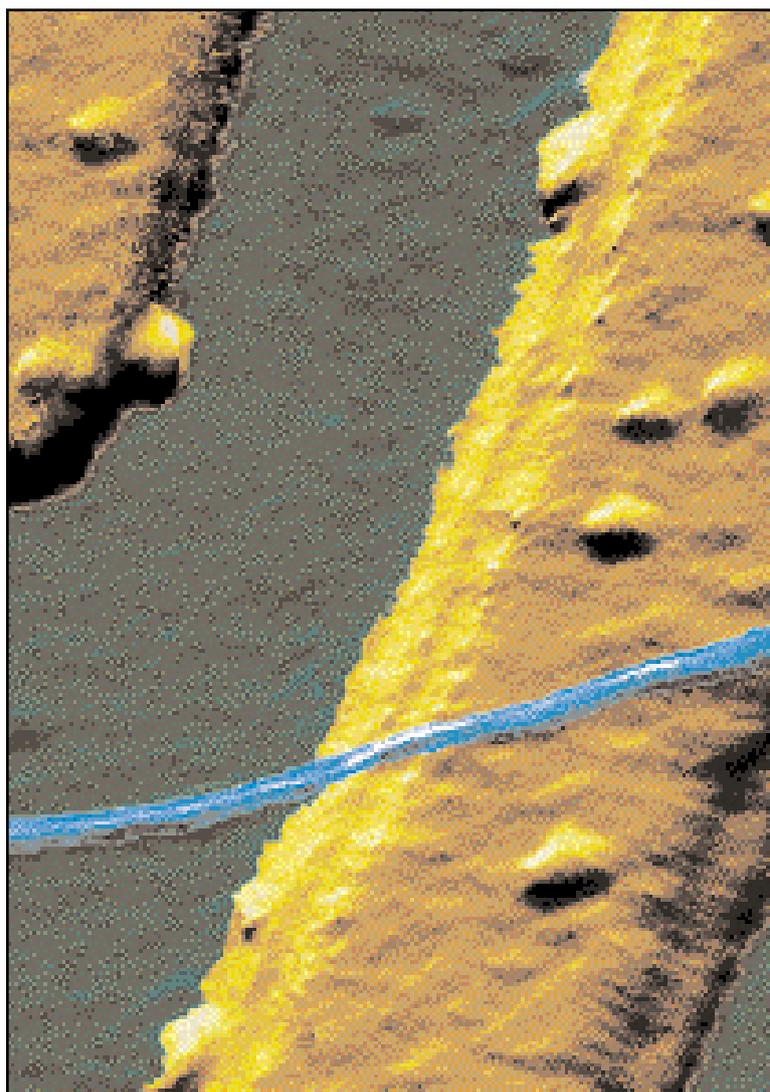
by Philip G. Collins and Phaedon Avouris

Nanotubes FOR Electronics

Nearly 10 years ago Sumio Iijima, sitting at an electron microscope at the NEC Fundamental Research Laboratory in Tsukuba, Japan, first noticed odd nanoscopic threads lying in a smear of soot. Made of pure carbon, as regular and symmetric as crystals, these exquisitely thin, impressively long macromolecules soon became known as nanotubes, and they have been the object of intense scientific study ever since.

Just recently, they have become a subject for engineering as well. Many of the extraordinary properties attributed to nanotubes—among them, superlative resilience, tensile strength and thermal stability—have fed fantastic predictions of microscopic robots, dent-resistant car bodies and earthquake-resistant buildings. The first products to use nanotubes, however, exploit none of these. Instead the earliest applications are electrical. Some General Motors cars already include plastic parts to which nanotubes were added; such plastic can be electrified during painting so that the paint will stick more readily. And two nanotube-based lighting and display products are well on their way to market.

In the long term, perhaps the most valuable applications will take further advantage of nanotubes' unique electronic properties. 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 below 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.

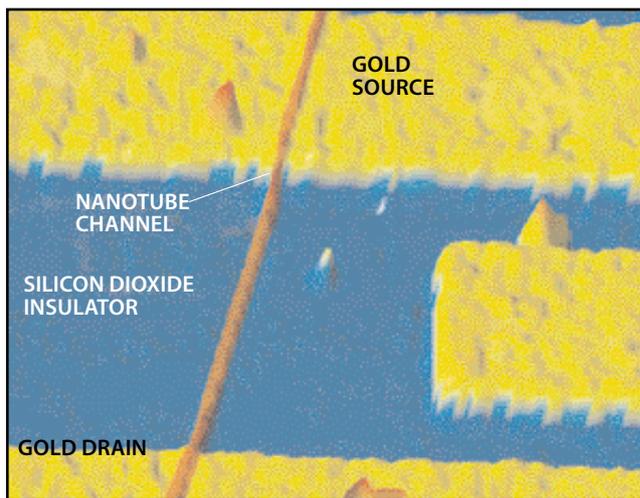
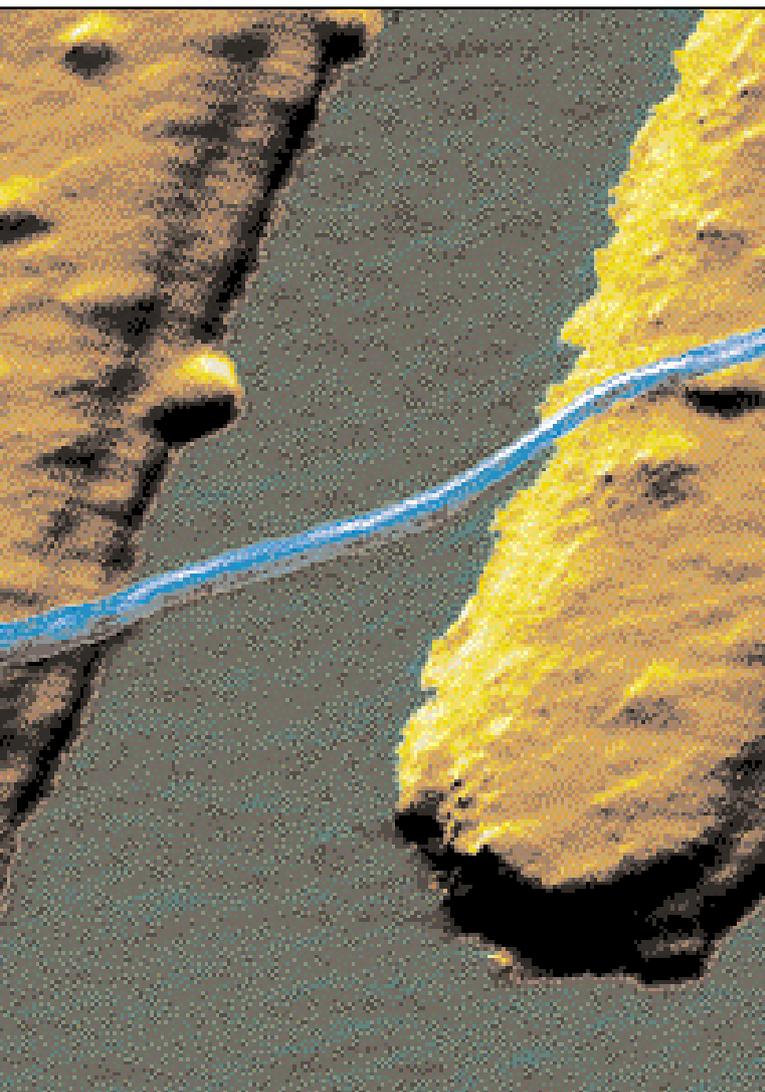
The first carbon nanotubes that Iijima observed back in 1991 were so-called multiwalled tubes: each contained a number of hollow cylinders of carbon atoms nested inside one another like Russian dolls. Two years later Iijima and Donald Bethune of IBM independently created single-walled nanotubes that were made of just one layer of carbon atoms. Both kinds of tubes are made in similar ways, and they have many similar properties—the most obvious being that they are exceedingly narrow and long. The single-walled variety, for example, is about one nanometer in diameter but can run thousands of nanometers in length.

What makes these tubes so stable is the strength with which carbon atoms bond to one another, which is also what makes diamond so hard. In diamond the carbon atoms link into four-sided tetrahedra, but in nanotubes the atoms arrange themselves in hexagonal rings like chicken wire. One sees the same pattern in graphite, and in fact a nanotube looks like a sheet (or several stacked sheets) of graphite rolled into a seamless cylinder. It is not known for certain how the atoms actually condense into tubes [see “Zap, Bake or

Blast,” on page 67], but it appears that they may grow by adding atoms to their ends, much as a knitter adds stitches to a sweater sleeve.

Tubes with a Twist

However they form, the composition and geometry of carbon nanotubes engender a unique electronic complexity. That is in part simply the result of size, because quantum physics governs at the nanometer scale. But graphite itself is a very unusual material. Whereas most electrical conductors can be classified as either metals or semiconductors, graphite is one of the rare materials known as a semimetal, delicately balanced in the transitional zone between the two. By combining graphite’s semimetallic properties with the quantum rules of energy levels and electron waves, carbon nanotubes emerge as truly exotic conductors.



MICROCHIPS OF THE FUTURE will require smaller wires and transistors than photolithography can produce today. Electrically conductive macromolecules of carbon that self-assemble into tubes (*top left*) are being tested as ultrafine wires (*left*) and as channels in experimental field-effect transistors (*above*).

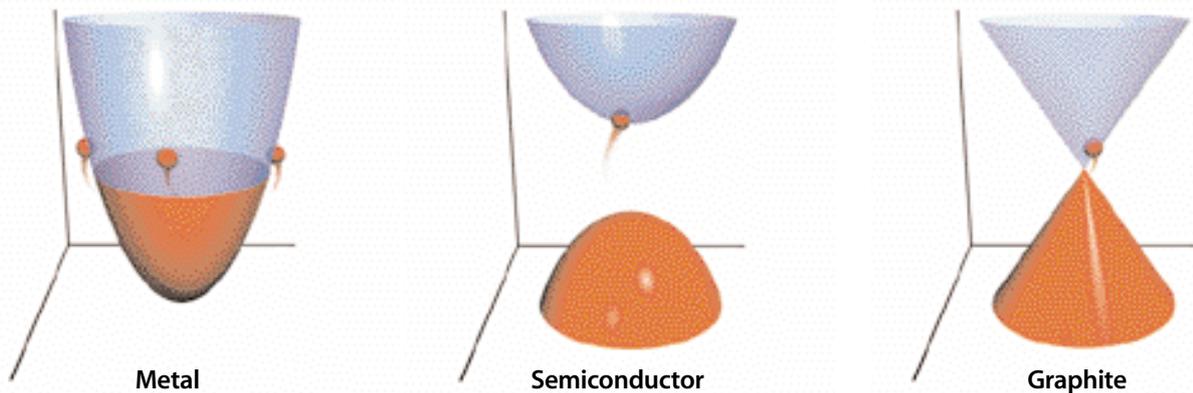
For example, one rule of the quantum world is that electrons behave like waves as well as particles, and electron waves can reinforce or cancel one another. As a consequence, an electron spreading around a nanotube’s circumference can completely cancel itself out; thus, only electrons with just the right wavelength remain. Out of all the possible electron wavelengths, or quantum states, available in a flat graphite sheet, only a tiny subset is allowed when we roll that sheet into a nanotube. That subset depends on the circumference of the nanotube, as well as whether the nanotube twists like a barbershop pole.

Slicing a few electron states from a simple metal or semiconductor won’t produce many surprises, but semimetals are much more sensitive materials, and that is where carbon nanotubes become interesting. In a graphite sheet, one particular electron state (which physicists call the Fermi point) gives graphite almost all of its conductivity; none of the electrons in other states are free to move about. Only one third of all carbon nanotubes combine the right diameter and degree of twist to include this special Fermi point in their subset of allowed states. These nanotubes are truly metallic nanowires.

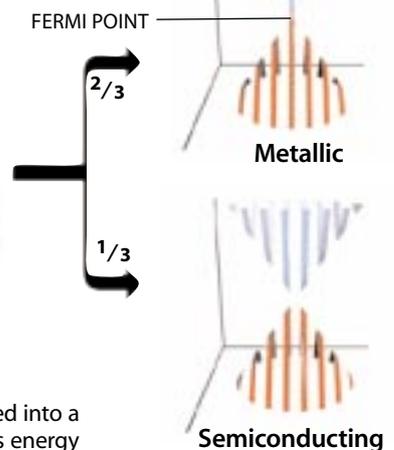
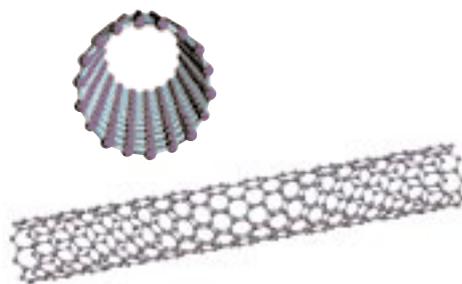
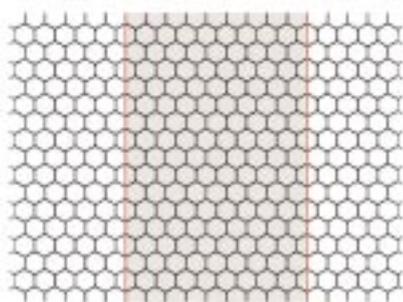
The remaining two thirds of nanotubes are semiconduc-

The Electrical Behavior of Nanotubes

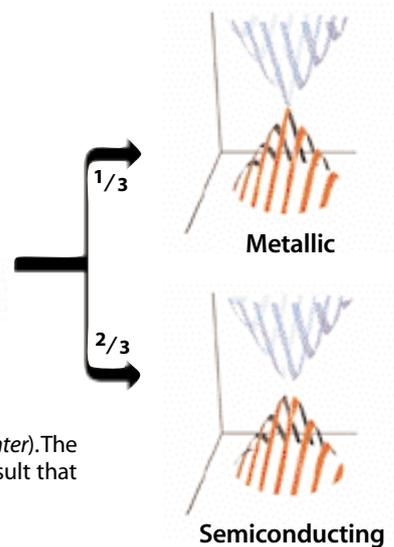
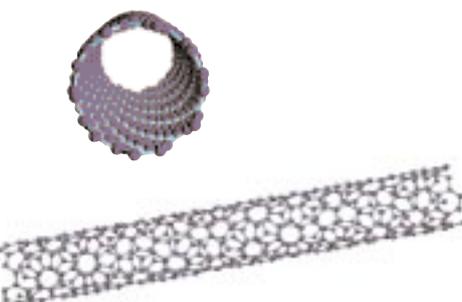
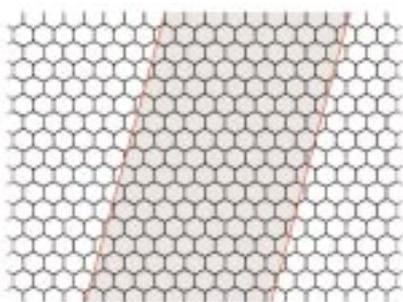
A Split Personality



ELECTRICAL PROPERTIES of a material depend on the separation between the collection of energy states that are filled by electrons (*red*) and the additional "conduction" states that are empty and available for electrons to hop into (*light blue*). Metals conduct electricity easily because there are so many electrons with easy access to adjacent conduction states. In semiconductors, electrons need an energy boost from light or an electrical field to jump the gap to the first available conduction state. The form of carbon known as graphite is a semimetal that just barely conducts, because without these external boosts, only a few electrons can access the narrow path to a conduction state.



STRAIGHT NANOTUBES look like a straight swath cut from a sheet of graphite (*left*) and rolled into a tube (*center*). The geometry of nanotubes limits electrons to a select few slices of graphite's energy states (*right*). Depending on the diameter of the tube, one of these slices can include the narrow path that joins electrons with conduction states. This special point, called the Fermi point, makes two thirds of the nanotubes metallic. Otherwise, if the slices miss the Fermi point, the nanotubes semiconduct.



TWISTED NANOTUBES, cut at an angle from graphite (*left*), look a bit like barbershop poles (*center*). The slices of allowed energy states for electrons (*right*) are similarly cut at an angle, with the result that about two thirds of twisted tubes miss the Fermi point and are semiconductors.

W. WAYT GIBBS (top and side rows); CLEO VILETT (sheets); J. CUMINGS AND A. ZETTL, University of California, Berkeley (tubes)

tors. That means that, like silicon, they do not pass current easily without an additional boost of energy. A burst of light or a voltage can knock electrons from valence states into conducting states where they can move about freely. The amount of energy needed depends on the separation between the two levels and is the so-called band gap of a semiconductor. It is semiconductors' band gaps that make them so useful in circuits, and by having a library of materials with different band gaps, engineers have been able to produce the vast array of electronic devices available today.

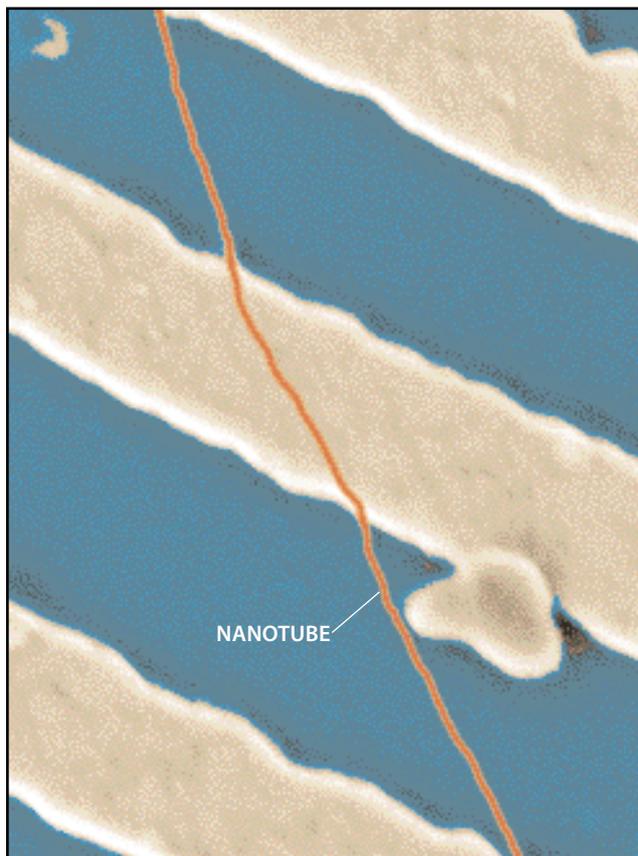
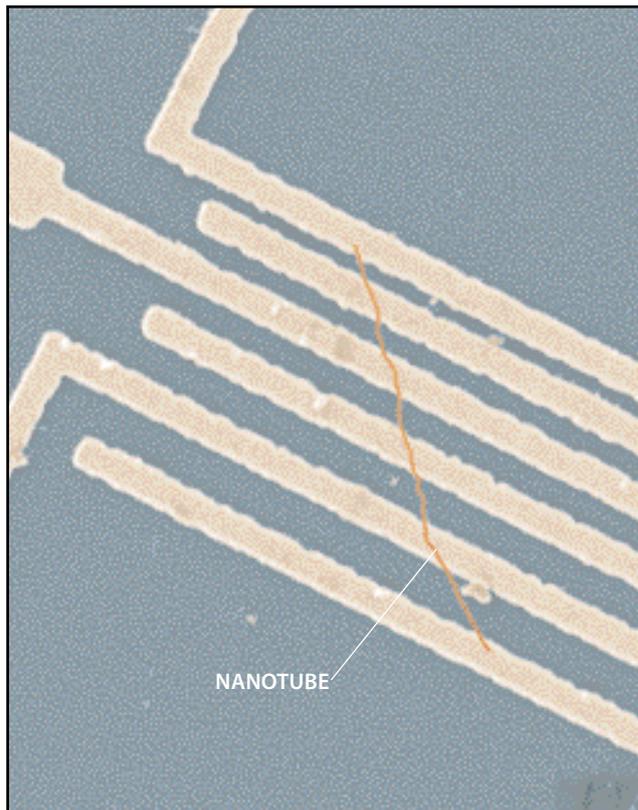
Carbon nanotubes don't all have the same band gap, because for every circumference there is a unique set of allowed valences and conduction states. The smallest-diameter nanotubes have very few states that are spaced far apart in energy. As nanotube diameters increase, more and more states are allowed and the spacing between them shrinks. In this way, different-size nanotubes can have band gaps as low as zero (like a metal), as high as the band gap of silicon, and almost anywhere in between. No other known material can be so easily tuned. Unfortunately, the growth of nanotubes currently gives a jumble of different geometries, and researchers are seeking improvements so that specific types of nanotubes can be guaranteed.

Fat multiwalled nanotubes may have even more complex behavior, because each layer in the tube has a slightly different geometry. If we could tailor their composition individually, we might one day make multiwalled tubes that are self-insulating or that carry multiple signals at once, like nanoscopic coaxial cables. Our understanding and control of nanotube growth still falls far short of these goals, but by incorporating nanotubes into working circuits, we have at least begun to unravel their basic properties.

Nanocircuits

Several research groups, including our own, have successfully built working electronic devices out of carbon nanotubes. Our field-effect transistors (FETs) use single semiconducting nanotubes between two metal electrodes as a channel through which electrons flow [see right illustration on page 63]. The current flowing in this channel can be switched on or off by applying voltages to a nearby third electrode. The nanotube-based devices operate at room temperature with electrical characteristics remarkably similar to off-the-shelf silicon devices. We and others have found, for example, that the gate electrode can change the conductivity of the nanotube channel in an FET by a factor of one million or more, comparable to silicon FETs. Because of its tiny size, however, the nanotube FET should switch reliably using much less power than a silicon-based device. Theorists predict that a truly nanoscale switch could run at clock speeds of one terahertz or more—1,000 times as fast as processors available today.

The fact that nanotubes come with a variety of band gaps and conductivities raises many intriguing possibilities for additional nanodevices. For example, our team and others have recently measured joined metallic and semiconducting nanotubes and shown that such junctions behave as diodes, permitting electricity to flow in only one direction. Theoretically, combinations of nanotubes with different band gaps could behave like light-emitting diodes and perhaps even nanoscopic lasers. It is now feasible to build a nanocircuit that has wires, switches and memory elements made entirely from



PHILIP G. COLLINS AND PHAEDON AVOINIS

AS ULTRATHIN WIRES, carbon nanotubes could free up space in microchips for more devices, as well as solving heat and stability problems. At a little over a nanometer in diameter, this single-walled nanotube makes lines drawn by state-of-the-art photolithography look huge in comparison.

nanotubes and other molecules. This kind of engineering on a molecular scale may eventually yield not only tiny versions of conventional devices but also new ones that exploit quantum effects.

We should emphasize, however, that so far our circuits have all been made one at a time and with great effort. The exact recipe for attaching a nanotube to metal electrodes varies among different research groups, but it requires combining traditional lithography for the electrodes and higher-resolution tools such as atomic force microscopes to locate and even position the nanotubes. This is obviously a long way from the massively parallel, complex and automated production of microchips from silicon on which the computer industry is built.

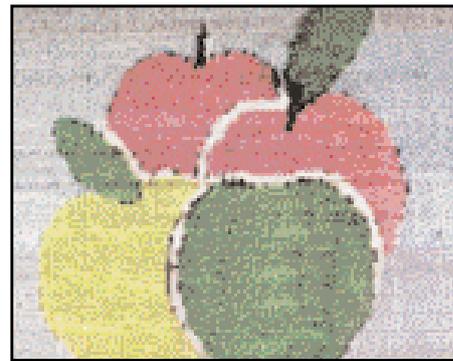
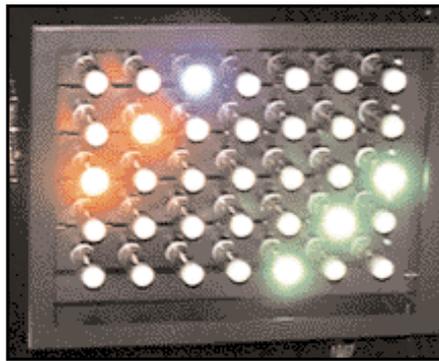
Before we can think about making more complex, nanotube-based circuitry, we must find ways to grow the nanotubes in specific locations, orientations, shapes and sizes. Scientists at Stanford University and elsewhere have demonstrated that by placing spots of nickel, iron or some other catalyst on a substrate, they can get nanotubes to grow where they want. A group at Harvard University has found a way to merge nanotubes with silicon nanowires, thus making connections to circuits fabricated by conventional means.

These are small steps, but already they raise the possibility of using carbon nanotubes as both the transistors and the interconnecting wires in microchip circuits. Such wires are currently about 250 nanometers in width and are made of metal. Engineers would like to make them much smaller, because then they could pack more devices into the same area. Two major problems have so far thwarted attempts to shrink metal wires further. First, there is as yet no good way to remove the heat produced by the devices, so packing them in more tightly will only lead to rapid overheating. Second, as metal wires get smaller, the gust of electrons moving through them becomes strong enough to bump the metal atoms around, and before long the wires fail like blown fuses.

In theory, nanotubes could solve both these problems. Scientists have predicted that carbon nanotubes would conduct heat nearly as well as diamond or sapphire, and preliminary experiments seem to confirm their prediction. So nanotubes could efficiently cool very dense arrays of devices. And because the bonds among carbon atoms are so much stronger than those in any metal, nanotubes can transport terrific amounts of electric current—the latest measurements show that a bundle of nanotubes one square centimeter in cross section could conduct about one billion amps. Such high currents would vaporize copper or gold.

Where Nanotubes Shine

Carbon nanotubes have a second interesting electronic behavior that engineers are now putting to use. In 1995 a research group at Rice University showed that when stood on end and electrified, carbon nanotubes will act just as lightning rods do, concentrating the electrical field at their tips. But whereas a lightning rod conducts an arc to the ground, a nano-



FIRST ELECTRONIC DEVICES to incorporate nanotubes include vacuum-tube lighting elements (*left*) and a full-color flat-panel display (*right*). Both products make use of nanotubes' ability to emit electrons at relatively low voltages without burning out, which translates into more efficient use of power and possibly greater durability.

tube emits electrons from its tip at a prodigious rate. Because they are so sharp, the nanotubes emit electrons at lower voltages than electrodes made from most other materials, and their strong carbon bonds allow nanotubes to operate for longer periods without damage.

Field emission, as this behavior is called, has long been seen as a potential multibillion-dollar technology for replacing bulky, inefficient televisions and computer monitors with equally bright but thinner and more power-efficient flat-panel displays. But the idea has always stumbled over the delicacy of existing field emitters. The hope is that nanotubes may at last remove this impediment and clear the way for an alternative to cathode-ray tubes and liquid-crystal panels.

It is surprisingly easy to make a high-current field emitter from nanotubes: just mix them into a composite paste with plastics, smear them onto an electrode, and apply voltage. Invariably some of the nanotubes in the layer will point toward the opposite electrode and will emit electrons. Groups at the Georgia Institute of Technology, Stanford and elsewhere have already found ways to grow clusters of upright nanotubes in neat little grids. At optimum density, such clusters can emit more than one amp per square centimeter, which is more than sufficient to light up the phosphors on a screen and is even powerful enough to drive microwave relays and high-frequency switches in cellular base stations.

Indeed, two companies have announced that they are developing products that use carbon nanotubes as field emitters. Ise Electronics in Ise, Japan, has used nanotube composites to make prototype vacuum-tube lamps in six colors that are twice as bright as conventional lightbulbs, longer-lived and at least 10 times more energy-efficient. The first prototype has run for well over 10,000 hours and has yet to fail. Engineers at Samsung in Seoul spread nanotubes in a thin film over control electronics and then put phosphor-coated glass on top to make a prototype flat-panel display. When they demonstrated the display last year, they were optimistic that the company could have the device—which will be as bright as a cathode-ray tube but will consume one tenth as much power—ready for production by 2001.

The third realm in which carbon nanotubes show special electronic properties is that of the very small, where size-dependent effects become important. At small enough scales, our simple concepts of wires with resistance dramatically fail and must be replaced with quantum-mechanical models. This is a realm that silicon technology is unlikely to reach, one

Three Ways to Make Nanotubes

Zap, Bake or Blast

Sumio Iijima may have been the first to see a nanotube, but he was undoubtedly not the first to make one. In fact, Neandertals may have made minuscule quantities of nanotubes, unwittingly, in the fires that warmed their caves. Split by heat, carbon atoms recombine however they can in soot, some in amorphous blobs but others in soccerball-shaped

spheres called buckyballs or in long cylindrical capsules called buckytubes or nanotubes. Scientists have discovered three ways to make soot that contains a reasonably high yield of nanotubes. So far, however, the three methods suffer some serious limitations: all produce mixtures of nanotubes with a wide range of lengths, many defects and a variety of twists to them.

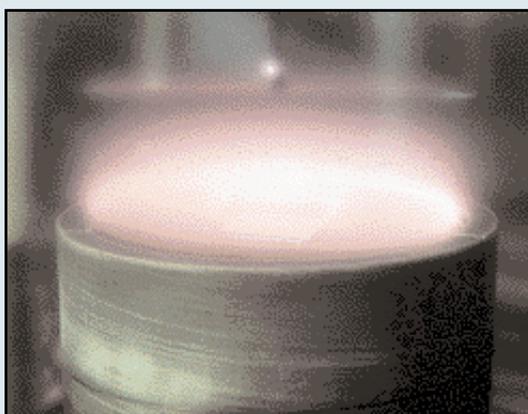
A BIG SPARK

In 1992 Thomas Ebbesen and Pulickel M. Ajayan of the NEC Fundamental Research Laboratory in Tsukuba, Japan, published the first method for making macroscopic quantities of nanotubes. It is almost Frankensteinian in its design: wire two graphite rods to a power supply, place them millimeters apart and throw the switch. As 100 amps of juice spark between the rods, carbon vaporizes into a hot plasma (right). Some of it recondenses in the form of nanotubes.

Typical yield: Up to 30 percent by weight

Advantages: High temperatures and metal catalysts added to the rods can produce both single-walled and multiwalled nanotubes with few or no structural defects.

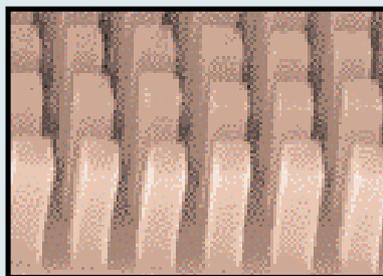
Limitations: Tubes tend to be short (50 microns or less) and deposited in random sizes and directions.



OAK RIDGE NATIONAL LABORATORY

A HOT GAS

Morinubo Endo of Shinshu University in Nagano, Japan, was the first to make nanotubes with this method, which is called chemical vapor deposition (CVD). This recipe is also fairly simple. Place a substrate in an oven, heat to 600 degrees Celsius and slowly add a carbon-bearing gas such as methane. As the gas decomposes, it frees up carbon atoms, which can recombine in the form of nanotubes.



HONGJIE DAI/Stanford University

control where the tubes form (left) and have been working to combine this controlled growth with standard silicon technology.

Typical yield: 20 to nearly 100 percent

Advantages: CVD is the easiest of the three methods to scale up to industrial production. It may be able to make nanotubes of great length, which is necessary for fibers to be used in composites.

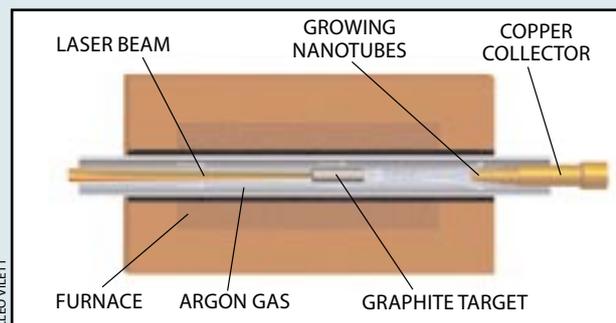
Jie Liu and his colleagues at Duke University recently invented a porous catalyst that they claim can convert almost all the carbon in a feed gas to nanotubes. By printing patterns of catalyst particles on the substrate, Hongjie Dai and his colleagues at Stanford University have been able to con-

essary for fibers to be used in composites. **Limitations:** Nanotubes made this way are usually multiwalled and are often riddled with defects. As a result, the tubes have only one tenth the tensile strength of those made by arc discharge.

A LASER BLAST

Richard Smalley and his co-workers at Rice University were blasting metal with intense laser pulses to produce fancier

metal molecules when the news broke about the discovery of nanotubes. They swapped the metal in their setup for graphite rods and soon produced carbon nanotubes by using laser pulses instead of electricity to generate the hot carbon gas from which nanotubes form (left). Trying various catalysts, the group hit on conditions that produce prodigious amounts of single-walled nanotubes.



CLEO VILETT

Typical yield: Up to 70 percent

Advantages: Produces primarily single-walled nanotubes, with a diameter range that can be controlled by varying the reaction temperature.

Limitations: This method is by far the most costly, because it requires very expensive lasers. —P.G.C. and P.A.

that may yield surprising new discoveries but will also require significantly more scientific research than will either nanocircuits or nanotube field-emission devices.

For example, researchers are currently debating exactly how electrons move along a nanotube. It appears that in defect-free nanotubes, electrons travel “ballistically”—that is, without any of the scattering that gives metal wires their re-

sistance. When electrons can travel long distances without scattering, they maintain their quantum states, which is the key to observing effects such as the interference between electron waves. A lack of scattering may also help explain why nanotubes appear to preserve the “spin” state of electrons as they surf along. (Electron spin is a quantum property, not a rotation.) Some researchers are now trying to make use of

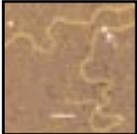
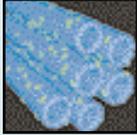
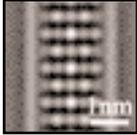


Other Uses for Nanotubes

Beyond Electronics

Feasibility Ratings

- 0 = Science Fiction
- 2 = Demonstrated
- 4 = Ready for Market

		THE IDEA	OBSTACLES	FEASIBILITY
	Chemical and Genetic Probes Tagged strand of DNA	A nanotube-tipped atomic force microscope can trace a strand of DNA and identify chemical markers that reveal which of several possible variants of a gene is present in the strand.	This is the only method yet invented for imaging the chemistry of a surface, but it is not yet used widely. So far it has been used only on relatively short pieces of DNA.	3
	Mechanical Memory Nonvolatile RAM	A screen of nanotubes laid on support blocks has been tested as a binary memory device, with voltages forcing some tubes to contact (the “on” state) and others to separate (the “off” state).	The switching speed of the device was not measured, but the speed limit for a mechanical memory is probably around one megahertz, which is much slower than conventional memory chips.	2
	Nanotweezers Pincers five microns long	Two nanotubes, attached to electrodes on a glass rod, can be opened and closed by changing voltage. Such tweezers have been used to pick up and move objects that are 500 nanometers in size.	Although the tweezers can pick up objects that are large compared with their width, nanotubes are so sticky that most objects can’t be released. And there are simpler ways to move such tiny objects.	2
	Supersensitive Sensors Oxygen sticks to tubes	Semiconducting nanotubes change their electrical resistance dramatically when exposed to alkalis, halogens and other gases at room temperature, raising hopes for better chemical sensors.	Nanotubes are exquisitely sensitive to so many things (including oxygen and water) that they may not be able to distinguish one chemical or gas from another.	3
	Hydrogen and Ion Storage Atoms in hollow core	Nanotubes might store hydrogen in their hollow centers and release it gradually in efficient and inexpensive fuel cells. They can also hold lithium ions, which could lead to longer-lived batteries.	So far the best reports indicate 6.5 percent hydrogen uptake, which is not quite dense enough to make fuel cells economical. The work with lithium ions is still preliminary.	1
	Sharper Scanning Microscope Individual IgM antibodies	Attached to the tip of a scanning probe microscope, nanotubes can boost the instruments’ lateral resolution by a factor of 10 or more, allowing clearer views of proteins and other large molecules.	Although commercially available, each tip is still made individually. The nanotube tips don’t improve vertical resolution, but they do allow imaging deep pits in nanostructures that were previously hidden.	4
	Superstrong Materials Nanotube stress test	Embedded into a composite, nanotubes have enormous resilience and tensile strength and could be used to make cars that bounce in a wreck or buildings that sway rather than crack in an earthquake.	Nanotubes still cost 10 to 1,000 times more than the carbon fibers currently used in composites. And nanotubes are so smooth that they slip out of the matrix, allowing it to fracture easily.	0

Compiled by W. Wayt Gibbs, staff writer

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this unusual behavior to construct “spintronic” devices that switch on or off in response to electrons’ spin, rather than merely to their charge, as electronic devices do.

Similarly, at the small size of a nanotube, the flow of electrons can be controlled with almost perfect precision. Scientists have recently demonstrated in nanotubes a phenomenon called Coulomb blockade, in which electrons strongly repulse attempts to insert more than one electron at a time onto a nanotube. This phenomenon may make it easier to build single-electron transistors, the ultimate in sensitive electronics. The same measurements, however, also highlight unanswered questions in physics today. When confined to such skinny, one-dimensional wires, electrons behave so strangely that they hardly seem like electrons anymore.

Thus, in time, nanotubes may yield not only smaller and better versions of existing devices but also completely novel ones that wholly depend on quantum effects. Of course, we will have to learn much more about these properties of nanotubes before we can rely on them. Some problems are already evident. We know that all molecular devices, nanotubes included, are highly susceptible to the noise caused by electrical, thermal and chemical fluctuations. Our experiments have also shown that contaminants (oxygen, for example) attaching to a nanotube can affect its electrical properties. That may be useful for creating exquisitely sensitive chemical detectors, but it is an obstacle to making single-molecule circuits. It is a major challenge to control contamination when single molecules can make a difference.

Nevertheless, with so many avenues of development under way, it seems clear that it is no longer a question of whether nanotubes will become useful components of the electronic machines of the future but merely a question of how and when.

Properties of Carbon Nanotubes

Going to Extremes

PROPERTY	SINGLE-WALLED NANOTUBES	BY COMPARISON
 Size	0.6 to 1.8 nanometer in diameter	Electron beam lithography can create lines 50 nm wide, a few nm thick
 Density	1.33 to 1.40 grams per cubic centimeter	Aluminum has a density of 2.7 g/cm ³
 Tensile Strength	45 billion pascals	High-strength steel alloys break at about 2 billion Pa
 Resilience	Can be bent at large angles and restraightened without damage	Metals and carbon fibers fracture at grain boundaries
 Current Carrying Capacity	Estimated at 1 billion amps per square centimeter	Copper wires burn out at about 1 million A/cm ²
 Field Emission	Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart	Molybdenum tips require fields of 50 to 100 V/μm and have very limited lifetimes
 Heat Transmission	Predicted to be as high as 6,000 watts per meter per kelvin at room temperature	Nearly pure diamond transmits 3,320 W/m-K
 Temperature Stability	Stable up to 2,800 degrees Celsius in vacuum, 750 degrees C in air	Metal wires in microchips melt at 600 to 1,000 degrees C
 Cost	\$1,500 per gram from BuckyUSA in Houston	Gold was selling for about \$10/g in October

LAURIE GRACE

The Authors

PHILIP G. COLLINS and PHAEDON AVOURIS are scientists at the IBM Thomas J. Watson Research Center, where they are investigating the electrical properties of various types of nanotubes. Collins holds degrees in physics and electrical engineering from the Massachusetts Institute of Technology and the University of California, Berkeley. Besides working as a physicist, he has spent two years as a high school teacher and is a professional whitewater-rafting guide. Avouris, who manages the nanoscience and nanotechnology group for IBM Research, was awarded the Feynman Prize for Molecular Nanotechnology. He is also an avid tropical ornithologist.

Further Information

CARBON NANOTUBES AS MOLECULAR QUANTUM WIRES. Cees Dekker in *Physics Today*, Vol. 52, No. 5, pages 22–28; May 1999.
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