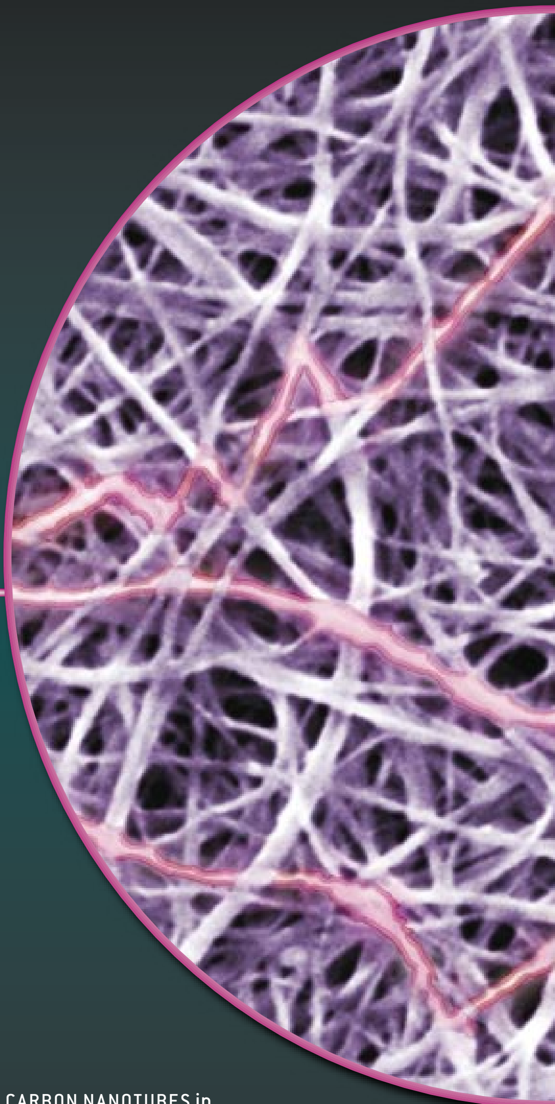
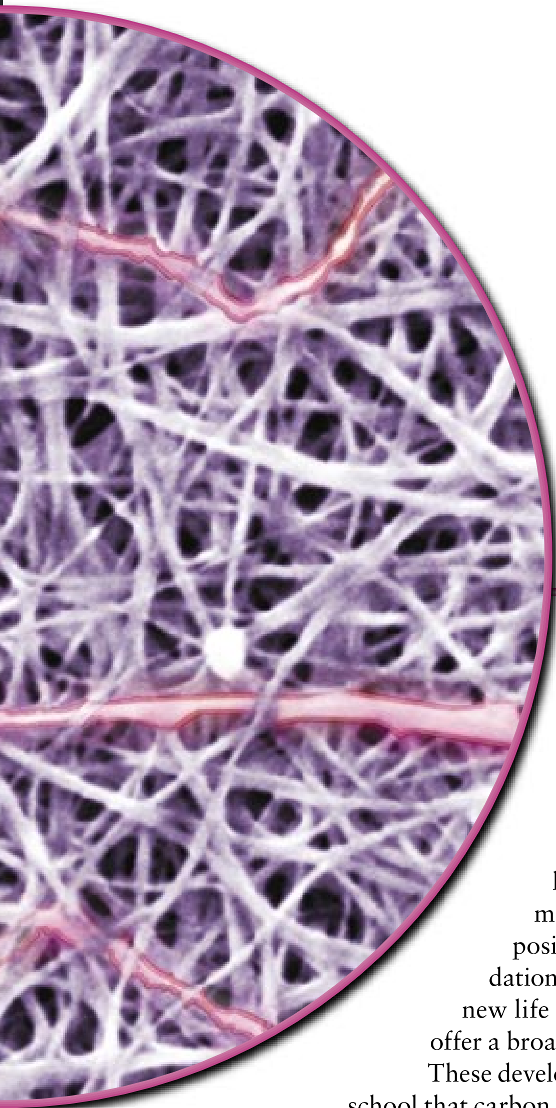
CARBON NANONETS

SPARK NEW ELECTRONICS



CARBON NANOTUBES in a weblike mesh ensure multiple alternative pathways for electrons (*pink highlights*), providing surefire electrical conduction. The entire field of view is 0.7 micron in diameter.

JOHN YORSTON *Carl Zeiss SMT* AND ANDREW PAUL LEONARD *APL Microscopic*; COLORIZED BY JEAN-FRANCOIS PODEVIN



Random networks of tiny carbon tubes could make possible low-cost, flexible devices such as "electronic paper" and printable solar cells

By George Gruner

In many classic science-fiction stories, alien life is based on silicon—the substance at the core of modern electronics technology—rather than on carbon, the fundamental building block of earthly biology. Scientists have even speculated that they might someday create silicon life-forms. Instead the opposite is starting to happen: carbon is serving as the foundation for electronic devices—and in the process is breathing new life into the quest for inexpensive, flexible products that offer a broad range of capabilities.

These developments may surprise those of us who learned in high school that carbon, in its familiar incarnations of diamond and graphite, does not conduct electricity well. During the past 15 years, however, researchers have discovered new forms of carbon: very small structures comprising a few hundred to 1,000 atoms, through which electrons travel with ease. Of particular interest is the carbon nanotube, a molecule that resembles rolled-up chicken wire, only the "wire" is a sheet of carbon atoms that is 100 million times as small as the version used for chicken coops.

Investigators have found that random networks of carbon nanotubes—called nanonets—can perform a variety of basic electronic functions. Using novel chemistry, researchers can make such networks mimic the conductive properties of metals such as copper or the less conductive characteristics of semiconductors such as silicon. These innovations have paved the way for this single material to assume different roles in electronic devices.

Further, engineers can construct such carbon-based devices by employing simple fabrication methods. Researchers can dissolve the tubes in a liquid and spray the resulting solution to form thin layers on, say, flexible plastic sheets. They can also lay or print these materials on other layers that have various electronic functions; for example, substances that emit light when a voltage is applied.

It takes little imagination to see how this kind of straightforward system could form the basis of many extremely cheap but handy products: "electronic paper" that could display information on sheets that roll up like conventional newsprint; chemical sensors; wearable electronic devices; solar cells that could be printed onto rooftop tiles; or scads of simple radio-frequency identification (RFID) sensors for monitoring warehouse or store inventories. For such applications, the expensive, lightning-fast processing power of integrated chips like Intel's Pentium processors or Samsung's video displays is not needed; rather R&D laboratories and start-up firms are racing to find technologies that can do the job well enough at low cost [*see table on page 83*].

Such exciting applications would make severe demands on today's electronic materials: they would need to be conductive, flexible, lightweight, transparent (at least for some applications, such as solar cells and displays) and inexpensive. But most conductors are metals, the majority of which are not transparent, whereas, as a rule, thin films of materials that are transparent, such as diamond, are insulators (they do not transmit electricity). Light can pass through one special class of metals, called metal oxides, however. The best known, indium tin oxide, is frequently used where engineers need see-through electrodes. But metal oxides are costly. They are also heavy and brittle, and their manufacture requires high processing temperatures and multibillion-dollar fabrication facilities.

Another alternative is an unusual category of plastics known as conducting polymers. Although common plastic substances are insulators, chemists have in recent decades managed to convert some polymers into semiconductors and even full-fledged conductors. Polymers can be produced using room-temperature techniques. Lightweight and flexible, they can easily take on multiple forms and are, of course, dirt cheap [see "Next Stretch for Plastic Electronics," by Graham P. Collins; Scientific American, August 2004]. On the downside, weak bonds hold together the atoms in most plastics. The bonds can break rather readily, which leads most polymers to degrade over time. Consider just how useful a solar cell would be if it failed after only a few warm, sunny days.

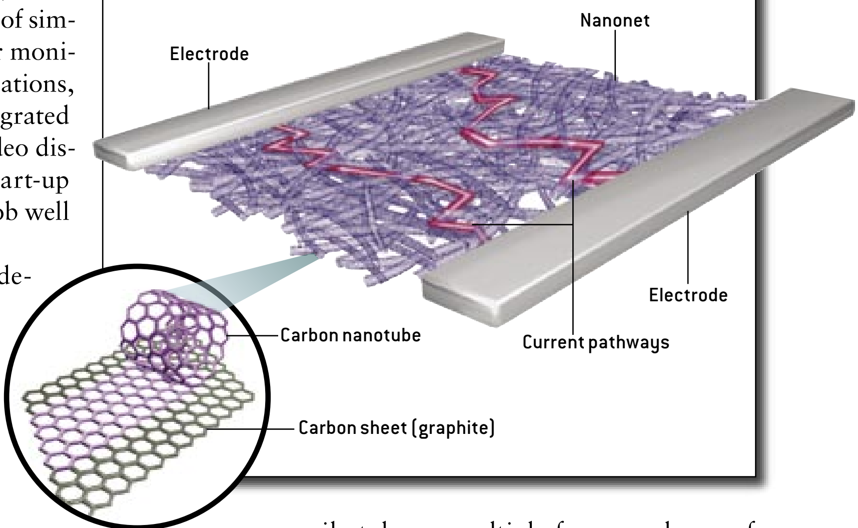
A Better Wire

ENTER CARBON-BASED NANOWIRES. Carbon nanotubes were first discovered several decades ago, but no one realized their value at the time. Then, in 1991, Japanese chemist Sumio Ijima of NEC Corporation rediscovered them. These tiny tubes of carbon have a diameter of around one nanometer—about the same as a strand of a DNA molecule [*see box above*]. The electrical conductivity of the tubes is comparable to that of copper and surpasses that of any polymer by several orders of magnitude. They can also carry more than 100 times more current than the best metals. Carbon nanotubes are, in addition, physically robust: they can be bent easily, they do not react with most chemicals and they resist damage from day-to-day use.

Manufacturers make nanotubes by reducing coal into its component atoms using the heat of an electric arc or a laser, which creates a so-called carbon plume. They then add catalysts to the plume, which promotes the formation of various types of carbon molecules. This relatively straightforward procedure produces what is essentially soot—carbon molecules in many forms, including spherical structures called

FROM NANOTUBES TO NANONETS

Thin networks of carbon nanotubes, or nanonets, can serve as electronic devices. Each nanotube is a one-atom-thick sheet of carbon, called graphite, rolled into a cylinder with a diameter of about a nanometer (*inset*)—approximately 50,000 times as small as the width of a human hair. Electric current passes through the interconnected tubes from one electrode to another.



JEAN-FRANCOIS PODEVIN

Overview/*Nanonet Electronics*

- Carbon nanotubes—minuscule cylinders of rolled-up carbon sheets—conduct electricity well, which could make them useful for many exciting electronic applications. But manufacturing products that use single tubes is expensive and suffers from significant reliability problems.
- Random networks of many carbon nanotubes, called nanonets, enable numerous basic electronic functions at low cost. The durable nature of nanonets also makes them suitable for portable devices.
- Carbon nanonets should find use in sensors, solar cells, electronic paper, and flexible touch screens and displays within a few years.

buckyballs as well as other "fullerenes" and carbon nanotubes. Fabricators must then laboriously separate the nanotubes out of the mixture. Techniques focus on separating out only the long, nearly perfect specimens that have a single "chicken wire" wall (rather than multiple, concentric walls). Suitable nanotubes are thus currently quite pricey, but makers are confident that costs will drop significantly if market demand rises enough to justify high-volume manufacturing facilities.

When a single nanotube is employed to build a transistor, the voltage-activated switch that is the workhorse of modern electronics [see "Nanotubes for Electronics," by Philip G. Collins and Phaedon Avouris; Scientific American, December 2000], the resulting device can easily outperform the transistors on the silicon chips in today's computers. But single carbon nanotubes will not replace silicon and copper in the foreseeable future. The main obstacle lies in their manufacturability, which is one of the most vexing problems afflicting nanotechnology's commercialization. Current devices based on a single nanotube can take days to make, because they often must be assembled by hand. Another difficulty is performance variability. Nanotubes come in slightly different shapes and forms, which affects their electrical attributes.

From One Wire to a Network

ALTHOUGH INDIVIDUAL TUBES differ from one to the next, researchers realized that this variation could be averaged out by using many tubes together—any shortcomings present in some of the tubes could be compensated for by better-performing counterparts. The simplest example is a random network of nanotubes [*see box on opposite page*]. Just as an interstate highway system can offer alternative routes when you encounter a traffic jam on one roadway, so, too, can a random assembly of electrically conducting nanotubes—a nanonet—speed the transmission of electrons by providing alternative pathways. Investigators soon established that these nearly two-dimensional random networks offered interesting properties in their own right.

First, the nanonet's many pathways and connections guarantee good electrical conductance between one electrode and another, despite possible manufacturing flaws. A good analogy is the freeway system that serves the Los Angeles metropolitan area. No one would want to attempt to traverse the City of Angels by hiking cross-country or driving the slow, stoplight-strewn surface roads; instead travelers take the freeway. The same concept applies to the nanonet, which allows electrons to jump on the tubes and move around on what is essentially a nanoscale freeway system. The multiple avenues provided by these networks also afford a considerable resistance to failure, or fault tolerance; if one route breaks from use, others are there to take up the slack.

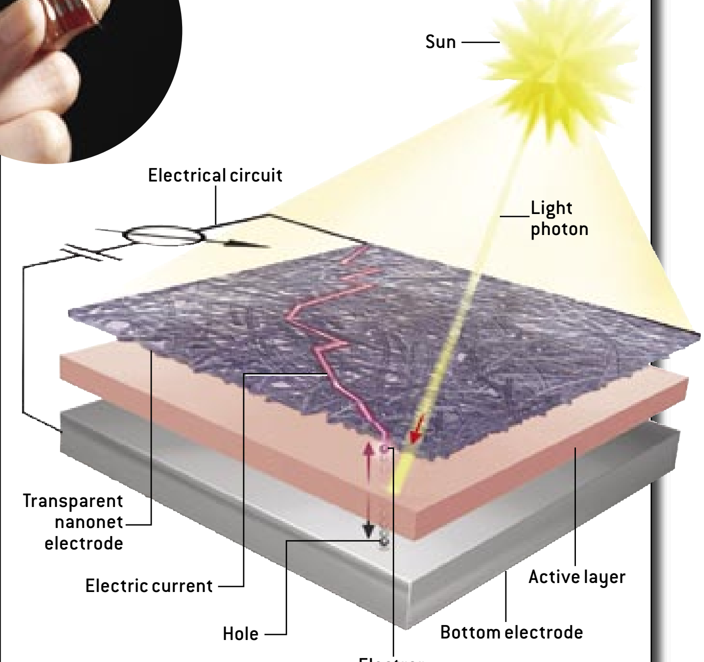
A conductive nanonet is in fact a simple example of the concept of percolation, which describes how objects, materials or electric currents move through a random medium. Imagine dropping pickup sticks on a tabletop one at a time. With only a few sticks, the chances of finding a connected pathway (by going from one stick to the next) from one end of the table to the other are slim. In fact, below a certain critical density of sticks, the odds drop to zero. But as the number of sticks increases, the pile will eventually surpass that critical density, the so-called percolation transition, where at first one and then more and more pathways form. If the pickup-stick approach were applied to copper wires on the tabletop, at some point the network would achieve electrical conduction across the table as well—with the current dependent on the density of the copper wires. Theorists studied this concept some time ago, and my group at the University of California, Los Angeles, was able to map out such a transition in networks of nanotubes.

Nanonets can be, in addition, highly transparent—an advantage in applications that require light transmission. Just as the freeway pavement covers only a small fraction of the natural terrain, a web of long and skinny wires allows passage of most of the incident light—a fraction that approaches 100 percent for what can be considered one-dimensional nanowires.

Finally, much like a spiderweb, a network of nanowires typically is more robust than the same material in undifferentiated bulk, which often tends to break when bent. These

CHEAPER SOLAR CELLS

Transparent and flexible carbon nanonet electrodes would be significantly cheaper than the rigid indium tin oxide electrodes used in today's solar cells (*shown in exploded view*). The carbon nanonets would conduct electric charges (negative electrons and positive "holes") dislodged by light photons from an active, charge-creating, layer of a semiconductor to an external circuit. A sample printed nanonet solar cell shows its bendability (*inset*).



JEAN-FRANCOIS PODEVIN; BRAD SWONETZ *Redux* (*solar cell, Stanford University*) characteristics make the nanonet architecture eminently suited for applications in which resistance to day-to-day use and misuse is important. Think about how many times you have dropped your cell phone or iPod.

Weaving a Nanonet

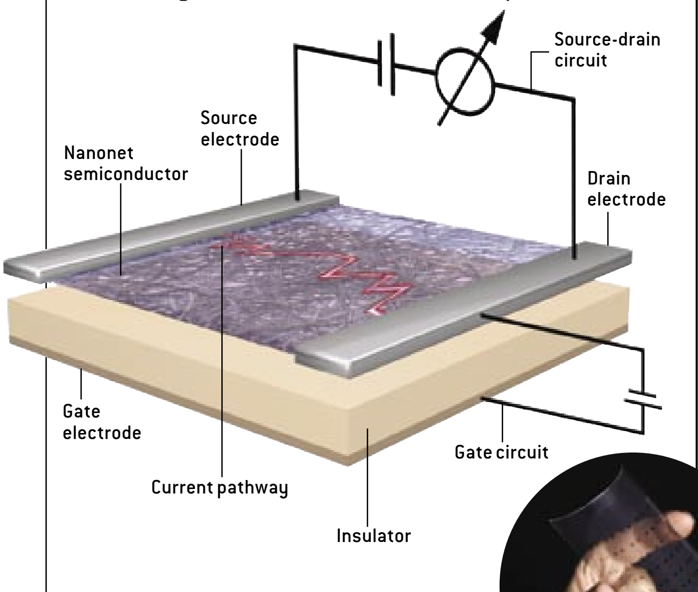
THESE PERFORMANCE BENEFITS augur well for the technology's potential in real-world applications, but any new replacement material must, of course, be more than competitive in terms of function and cost with current materials. Nanotube films initially made a couple of years ago—by my team, by a group led by physicist Siegmar Roth at the Max Planck Institute for Solid State Research in Stuttgart, Germany, and by one at the University of Texas at Austin—were not up to the task. Finding the optimal processing routes and the most advantageous way to deposit the tubes onto surfaces were not trivial problems.

Clearly, one cannot fabricate thin films of such networks by merely throwing down a tube at a time like playing pickup sticks; another strategy is needed. One might, for instance, dissolve the tubes in a solvent (water, alcohol, organic liquids) and then spray the resulting fluid onto a surface, but that is not as easy as it sounds. When mixed in a liquid, the tubes tend to bundle together, requiring a chemical additive to keep them apart. Some agents, called surfactants (soaps), accomplish this job by completely surrounding the tubes. But surfactants, if they remain on the tubes after they are sprayed onto a surface, impede the flow of electrons between tubes (blocking the freeway ramps, so to speak). Through steady trial-and-error efforts with innumerable solvents, surfactants and processing procedures, however, researchers have created simple (room-temperature) avenues to make such thin films of nanotube networks. At the moment, a method pioneered by my team and a group led by chemist Andrew Rinzler at the University of Florida yields films that have the lowest electrical resistance and thus the best operating performance to date among nanonet-based devices.

As researchers experimented with the conductivity of the tubes, they learned that the material could be transparent, a property that is important for applications such as displays and solar cells. The discovery that carbon nanonets are transparent to light came about as a by-product of research on their conductivity. The first indication that nanonets could be clear arose in 2001, when my former postdoctoral associate Leonardo Degiorgi and his group at the Swiss Federal Institute of Technology in Zurich, along with physicist David Tanner and his co-workers at the University of Florida, studied their optical characteristics. To measure nanonet conductivity precisely, they fabricated thick films: these were too deep to transmit light, but their data led them to conclude that a thinner film would be both transparent and a good conductor. After these groups made this determination, Rinzler's team (collaborating with Katalin Kamarás and her colleagues at the Central Institute of Physics in Budapest) and mine at U.C.L.A. followed up with direct measurements of a nanonet film's optical transparency. Today scientists can fabricate tailor-made films with different levels of transparency and electrical conductivity by changing the thickness of the films.

TRANSPARENT TRANSISTORS

Carbon nanonet films, tailored to perform like semiconductors, can serve as the basis for field-effect transistors—the building blocks of computers, cellular phones and other digital devices. This switchlike mechanism (*shown in exploded view*) uses a small electric voltage provided by the gate electrode to greatly boost the current in the source-drain circuit. In the inset, a technician bends a plastic sheet onto which an array of see-through nanonet transistors has been printed.



Nanonet Transistors

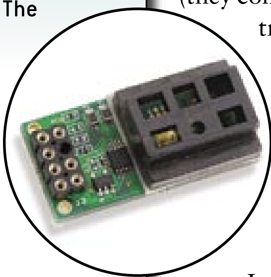
RESEARCHERS SOON TURNED their attention from making nanonet conductors to nanonet semiconductors that could serve as the basis for transistors. A transistor requires materials whose conductivity changes greatly in response to only small incremental inputs, such as altering an electric field [*see box at left*].

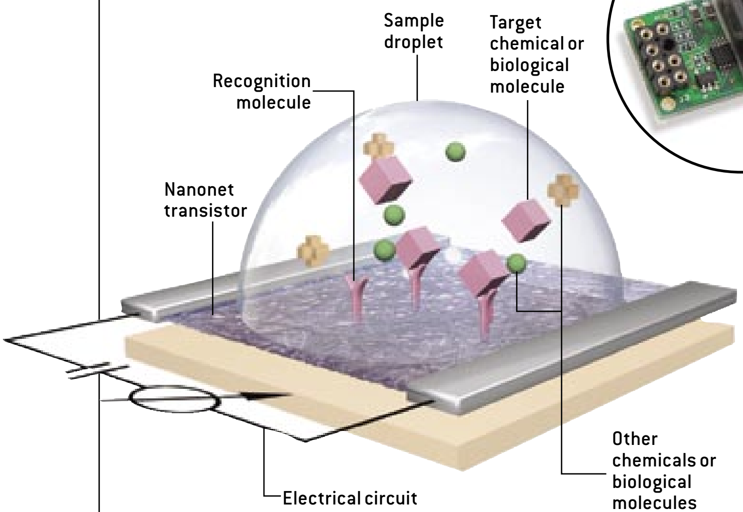
The notion that carbon nanotube networks could serve as the backbone of thin-film field-effect transistors emerged around seven years ago. Thereafter, progress was relatively rapid—with advances in creating nanonets on flexible substrates, demonstrating the transparency of the devices, coming in short order. Working in parallel, my R&D group at Nanomix, a start-up firm in Emeryville, Calif., where I served as chief scientist, and a research team at the Naval Research Laboratory in Washington, D.C., led by materials scientist Eric Snow, produced nanonet transistors in 2003. But these devices were formed on rigid glass substrates at processing temperatures of 900 degrees Celsius—too hot for use with flexible plastic substrates that melt at

JEAN-FRANCOIS PODEVIN; BRAD SWONETZ *Redux* (*transistor*, *Unidym*)

LOW-COST SENSORS

A nanonet device can become a sensor with the addition of "recognition molecules" that react with a target chemical or biological molecule. When the target binds to a recognition molecule, it alters the sensor's electrical output. Such devices can detect many chemicals, including a blood-borne cancer marker called prostate specific antigen (PSA) and, soon, microorganisms such as the anthrax bacterium, a potential bioweapon. Arrays of nanonet sensors, each with different recognition molecules, could cheaply detect specific genes or proteins for medical purposes. The inset shows a nanonet-based detector chip (*black*) on a printed circuit board.





120 degrees C. Nanomix researchers Keith Bradley and Jean-Christophe Gabriel, in collaboration with my U.C.L.A. team, manufactured the first flexible nanotube network transistors on plastic in 2003. Soon afterward, my colleagues and I at U.C.L.A., working with Roth's group at the Max Planck Institute, managed to fabricate devices that were also transparent, making them suitable for applications such as portable visual displays. Physicist John Rogers and his colleagues at the University of Illinois achieved similar success only a few months later. Although these field-effect transistors operated at fast rates—the key metric for such devices—other necessary characteristics, such as low-voltage function, were lacking. The goal was to run the devices at voltages less than those standard batteries can provide to save power, but this feat was attained only recently by Rogers and by chemist Tobin Marks of Northwestern University, who employed specially made polymers to insulate the devices' conductive parts.

Nanonets in Action

CARBON NANONETS CAN OFFER distinct advantages in many portable products, a conclusion that becomes more obvious when one compares them with some of the current contenders for these applications, including films composed of organic or polymeric metals and some semiconductors. For these uses, electronic materials must exhibit good electrical conductance (otherwise, applied current heats them up, resulting in power losses) and high optical transparency (because the viewer of a display, for example, needs to see the layers that lie underneath).

Such substances will enable the development of what people variously call printed, plastic, disposable or macroelectronic products. One example is the photovoltaic cell. Typical solar cells made of single-crystal silicon have excellent performance (they convert as much as 18 percent of incoming light into electricity) but are bulky, heavy and costly to manufacture. Instead imagine a razor-thin solar cell that, though less efficient (converting only 5 or 6 percent of incoming light), is significantly cheaper to fabricate and offers the potential for easy mass production of large-area systems, both of which can compensate for the material's lower performance levels [*see box on page 79*].

In a solar cell, incoming sunlight dislodges electrons and their positively charged counterparts, called holes, in the middle layer of the device. The electrons then migrate to one electrode, power some electrical load and return to the holes via another electrode to complete the circuit. Several companies are working to perfect a cell's active (charge-creating) layers using advanced polymers and other substances that are transparent and flexible. Together with Michael McGehee's materials science group at Stanford University and physical chemist Niyazi Serdar Sariciftci of the University of Linz in Austria, my U.C.L.A. team has produced flexible, proof-of-concept solar cells with nanonet electrodes that exhibit performance comparable to that of indium tin oxide electrodes.

Also under consideration are nanonet-based films that would lie at the heart of an inexpensive, flexible and lightweight touch screen or visual display. A touch screen, for instance, consists of two sheets of electrodes separated by insulating spacers. When a finger touches the top sheet at some point, the electrodes there meet, completing an electrical circuit specific for that location that is formed by a pattern of smooth, thin layers of conductive materials that have been imprinted on the bottom sheet. In collaboration with Richard Kaner's group at U.C.L.A., my team has fabricated and tested proof-of-concept devices based on nanonets.

Nanonets also work in light-emitting diodes, which resemble photovoltaics that run in reverse so that they create

THE AUTHOR

GEORGE GRUNER, a Distinguished Professor of Physics at the University of California, Los Angeles, investigates fundamental issues relating to nanoscale phenomena. He has served as the chief technology officer at Nanomix in Emeryville, Calif., and he is founder of Unidym in Menlo Park, Calif.; both companies concentrate on developing novel applications of nanotechnology. Gruner's interests include skiing, classical music and technology assessment—not necessarily in that order.

His research is supported by the National Science Foundation.

JEAN-FRANCOIS PODEVIN; NANOMIX "SENSATION" (*sensor*) light when electricity passes between the electrodes. In collaboration with Marks's group at Northwestern, my team has recently demonstrated proof-of-concept light-emitting diodes with excellent performance (sufficient to meet the requirements for use in televisions, for example), as has a research group at the University of Montreal led by Richard Martel.

Transistors made from nanonets will, in addition, find use in printed electronics. Tests indicate that the operating speed of carbon nanonets lags somewhat behind that of crystalline silicon, from which most integrated chips are fabricated, but their conductivity and durability advantages over polymers make them attractive to device manufacturers. Although nanotube films cannot yet work in laptop computers or television sets, they are competitive in many other products—especially those that require a material that is cheap, flexible, lightweight, environmentally friendly and resistant to abuse. The first such application is expected to be large-area visual displays, called active-matrix displays. The transistors in a display must run rapidly so that the images can be readily refreshed.

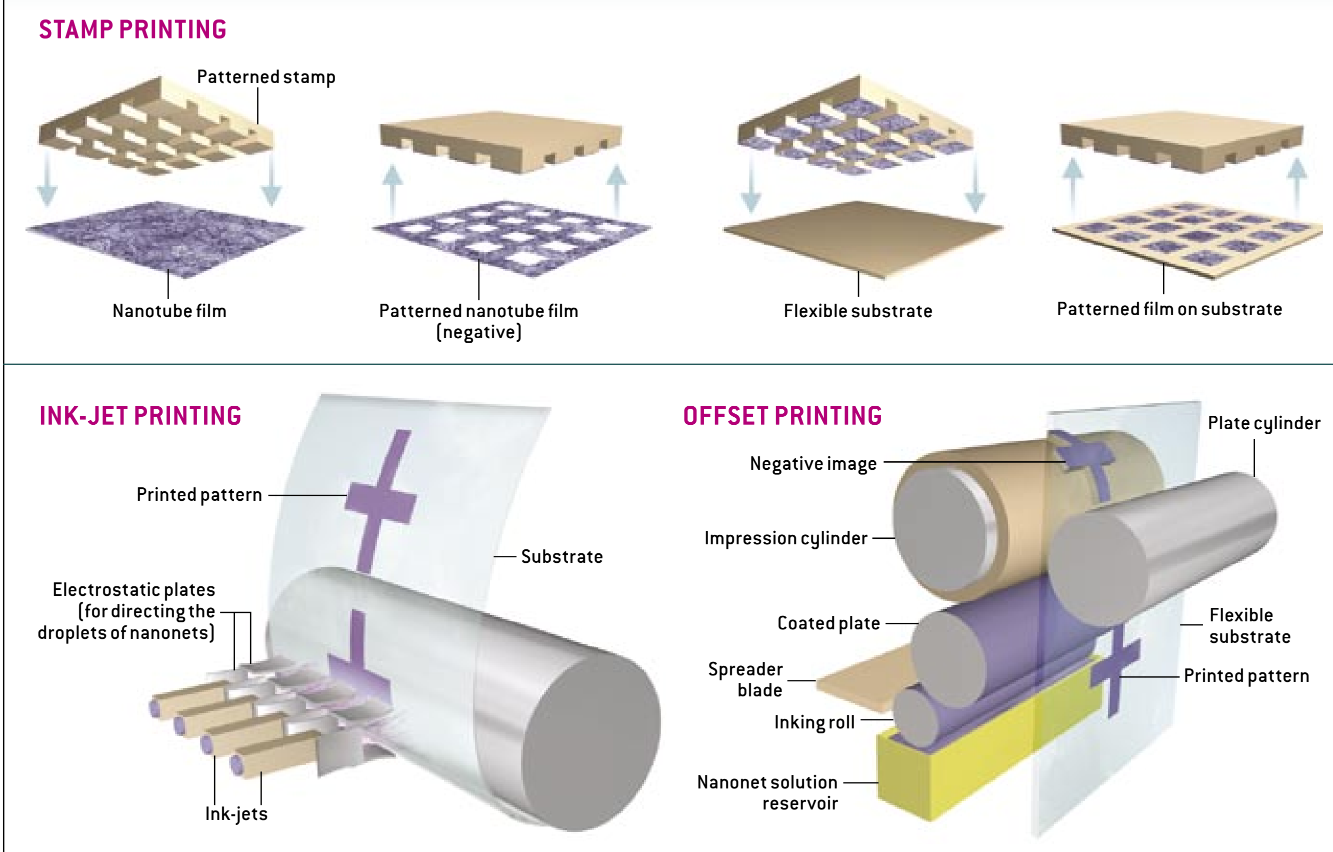
Of course, the kind of portable devices that will use these displays will need power sources as well—cheap, lightweight, razor-thin and disposable batteries and supercapacitors. Nanonets could also play an important role in such power devices, serving not only as electrodes but as high-surface-area components for collecting electric charge to store it for later discharge.

Many Pathways to Take

THE NASCENT CARBON NANONET industry has only just begun to perfect this fledgling technology. There is little doubt that the recent feasibility studies that I have described will soon be followed by working prototypes and eventually products based on those new devices. Today the industry is at the stage where the silicon chip business was half a century ago. The nanotubes are improving steadily, and researchers are successfully sorting those that conduct electricity as well as

PRINTING A NANONET

Prospective makers of products based on carbon nanonets are developing several inexpensive ways to "print" an engineered pattern of the material onto a flexible polymer surface to produce, for example, an electronic circuit. The simplest method resembles using an ink pad and a stamp (*top*). A patterned stamp comes into contact with a nanonet layer, parts of which stick to the stamp's bottommost surface. The primed stamp presses down on the surface of a substrate, printing the nanonet pattern onto it. Manufacturers are also working on two mass-production techniques, including the use of standard ink-jets (*bottom left*) to spray a liquid containing dispersed nanotubes onto substrates, and a variant of offset printing, in which a nanonet solution substitutes for ink (*bottom right*).



JEAN-FRANCOIS PODEVIN

Carbon Nanonet Research and Product Development

Many R&D organizations are producing or working to develop carbon nanotube materials, carbon nanonet films and the electronic devices that incorporate them. A new technology typically passes through the following sequence of developmental stages: concept, R&D, proof of concept, prototype, product development and production.

ORGANIZATION	PRODUCT FOCUS	STATUS
HIGH-GRADE MATERIALS FOR ELECTRONICS		
CarboLex, Lexington, Ky. (www.carbolex.com)	Electric arc– and chemical vapor deposition (CVD)–based fabrication	Production
Carbon Nanotechnologies, Houston (www.cnanotech.com)	CVD- and carbon monoxide–based fabrication	Production
Carbon Solutions, Riverside, Calif. (www.carbonsolution.com)	Electric arc–based fabrication	Production
SouthWest NanoTechnologies, Norman, Okla. (www.swnano.com)	CVD-produced specialty nanotubes	Production
Thomas Swan, Consett, England (www.thomas-swan.co.uk)	High-volume CVD-based fabrication	Production
TRANSPARENT FILMS		
Battelle Memorial Institute, Columbus, Ohio (www.battelle.org)	Transparent coatings	R&D
Eikos, Franklin, Mass. (www.eikos.com)	Conducting ink	Product development
Eastman Kodak, Rochester, N.Y. (www.kodak.com)	Transparent optical coatings	R&D, prototype
Unidym, Menlo Park, Calif. (www.unidym.com)	Films for touch screens, solar cells, light-emitting diodes	Product development
DEVICES		
DuPont, Wilmington, Del. (www.dupont.com)	Transparent electronics	R&D
IBM, Armonk, N.Y. (www.ibm.com)	Computer-compatible transistors and interconnects	R&D
Intel, Santa Clara, Calif. (www.intel.com)	Interconnects	R&D
Motorola, Schaumburg, Ill. (www.motorola.com)	Biological and chemical sensors	Prototype
Nanomix, Emeryville, Calif. (www.nano.com)	Chemical and biological sensors	Product development, R&D
Nantero, Woburn, Mass. (www.nantero.com)	Novel memory technology	Prototype
Samsung, Seoul, South Korea (www.samsung.com)	Displays	R&D
Unidym (*see above*)	Printed electronics for displays	Proof of concept

metals do from those that are semiconductors, which will further better device performance. Meanwhile investigators have made progress on a process that resembles silicon doping, in which special molecules are attached to the tubes to finely alter their electrical properties. Many observers believe that it is only a matter of time before such films exceed the performance of traditional metals and start to make inroads into silicon-based digital electronics technology.

Carbon nanonets have just recently left the realm of science fiction and entered that of practical reality. Like silicon, this budding technology is highly unlikely to lead to artificial life anytime soon, but it has every chance of enabling innovative products that in the not too distant future will improve our everyday lives. SA

MORE TO EXPLORE

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