LICUIT

RESEARCHERS HAVE BUILT NANOTRANSISTORS AND NANOWIRES. NOW THEY JUST NEED TO FIND A WAY TO PUT THEM ALL TOGETHER

BY CHARLES M. LIEBER

NANOWIRES, each about five to 10 nanometers in diameter, may represent the future of electronics. They are the brown lines, made of indium phosphide, connecting the gold electrodes in this micrograph. These wires have been put to truly diverse uses—as memory and logic and as arrays of light-emitting diodes.

Do we really need to keep on making circuits smaller? The miniaturization of silicon microelectronics seems so inexorable that the question seldom comes up-except maybe when we buy a new computer, only to find that it becomes obsolete by the time we leave the store. A state-of-theart microprocessor today has more than 40 million transistors; by 2015 it could have nearly five billion. Yet within the next two decades this dramatic march forward will run up against scientific, technical and economic limits. A first reaction might be, So what? Aren't five billion transistors enough already?

Yet when actually confronted with those limits, people will no doubt want to go beyond them. Those of us who work to keep computer power growing are motivated in part by the sheer challenge of discovering and conquering unknown territory. But we also see the potential for a revolution in mediels of organization. The basic building block is usually the transistor or its nanoequivalent—a switch that can turn an electric current on or off as well as amplify signals. In microelectronics, transistors are made out of chunks of semiconductor-a material, such as impure silicon, that can be manipulated to flip between conducting and nonconducting states. In nanoelectronics, transistors might be organic molecules or nanoscale inorganic structures.

The next level of organization is the interconnection—the wires that link transistors together in order to perform arithmetic or logical operations. In microelectronics, wires are metal lines typically hundreds of nanometers to tens of microns in width deposited onto the silicon; in nanoelectronics, they are nanotubes or other wires as narrow as one nanometer.

At the top level is what engineers call architecture—the over-

The use of molecules for electronic devices remained theoretical until a recent confluence of advances in chemistry, physics and engineering.

cine and so many other fields, as extreme miniaturization enables people and machines to interact in ways that are not possible with existing technology.

As the word suggests, microelectronics involves components that measure roughly one micron on a side (although lately the components have shrunk to a size of almost 100 nanometers). Going beyond microelectronics means more than simply shrinking components by a factor of 10 to 1,000. It also involves a paradigm shift for how we think about putting everything together.

Microelectronics and nanoelectronics both entail three lev-

of the lower-level details. Nanoelectronics researchers have not quite gotten to the point of testing different architectures, but we do know what abilities they will be able to exploit and what weaknesses they will need to compensate for. In other ways, however, microelectronics and nanoelec-

all way the transistors are interconnected, so that the circuit can

plug into a computer or other system and operate independently

tronics could not be more different. To go from one to the other, many believe, will require a shift from top-down manufacturing to a bottom-up approach. To build a silicon chip today, fabrication plants start with a silicon crystal, lay down a pattern using a photographic technique known as lithography, and etch away the unwanted material using acid or plasma. That procedure simply doesn't have the precision for devices that are mere nanometers in width. Instead researchers use the methods of synthetic chemistry to produce building blocks by the mole (6×10^{23} pieces) and assemble a portion of them into progressively larger structures. So far the progress has been impressive. But if this research is a climb up Mount Everest, we have barely just reached the base camp.

Overview/Nanoelectronics

- Silicon chips, circuit boards, soldering irons: these are the icons of modern electronics. But the electronics of the future may look more like a chemistry set. Conventional techniques can shrink circuits only so far; engineers will soon need to shift to a whole new way of organizing and assembling electronics. One day your computer may be built in a beaker.
- Researchers have created nanometer-scale electronic components-transistors, diodes, relays, logic gatesfrom organic molecules, carbon nanotubes and semiconductor nanowires. Now the challenge is to wire these tiny components together.
- Unlike conventional circuit design, which proceeds from blueprint to photographic pattern to chip, nanocircuit design will probably begin with the chip—a haphazard jumble of as many as 1024 components and wires, not all of which will even work—and gradually sculpt it into a useful device.

Smallifying Machines

THE USE OF MOLECULES for electronic devices was suggested more than a quarter of a century ago in a seminal paper by Avi Aviram of IBM and Mark A. Ratner of Northwestern University. By tailoring the atomic structures of organic molecules, they proposed, it should be possible to concoct a transistorlike device. But their ideas remained largely theoretical until a recent confluence of advances in chemistry, physics and engineering.

Of all the groups that have turned Aviram and Ratner's

NANOTRANSISTORS ROTOXANE BENZENETHIOL MOLECULAR TRANSISTORS could be the building blocks of electronics on the nanometer scale. Each of the two molecules shown here conducts electricity like a tiny wire once a SWITCH OFF chemical reaction-SWITCH OFF oxidation reduction-alters its atomic configuration SWITCH ON and switches it on. In the SWITCH ON diagram, each stick ELECTRON represents a chemical bond: each intersection of two sticks represents a carbon atom; and each ball represents an atom other than carbon.

ideas into reality, two teams—one at the University of California at Los Angeles and Hewlett-Packard, the other at Yale, Rice and Pennsylvania State universities—stand out. Within the past year, both have demonstrated that thousands of molecules clustered together can carry electrons from one metal electrode to another. Each molecule is about 0.5 nanometer wide and one or more nanometers long. Both groups have shown that the clusters can behave as on/off switches and might thus be usable in computer memory; once on, they will stay on for 10 minutes or so [see "Computing with Molecules," by Mark A. Reed and James M. Tour; Scientific American, June 2000]. That may not sound like a long time, but computer memory typically loses its information instantly when the power is turned off; even when the power is on, the stored information leaks away and must be "refreshed" every 0.1 second or so.

Although the details differ, the switching mechanism for both molecules is believed to involve a well-understood chemical reaction, oxidation reduction, in which electrons shuffle among atoms within the molecule. The reaction puts a twist in the molecule, blocking electrons as surely as a kink in a hose blocks water [see illustration above]. In the "on" position, the clusters of molecules may conduct electricity as much as 1,000 times better than in the "off" position. That ratio is actually rather low compared with that of typical semiconductor transistors, whose conductivity varies a millionfold. Researchers are now looking for other molecules with even better switching properties and are also working to understand the switching process itself.

My own research group at Harvard University is one of several that have focused not on organic molecules but on long, thin inorganic wires. The best-known example is the carbon nanotube, which is typically about 1.4 nanometers in diameter [see "Nanotubes for Electronics," by Philip G. Collins and Phaedon Avouris; Scientific American, December 2000]. Not only can these nanoscale wires carry much more current, atom for atom, than ordinary metal wires, they can also act as tiny transistors. By functioning both as interconnections and as components, nanowires kill two birds with one stone. Another advantage is that they can exploit the same basic physics as standard silicon microelectronics, which makes them easier to understand and manipulate.

In 1997 Cees Dekker's group at the Delft University of Technology in the Netherlands and Paul L. McEuen's group, then at the University of California at Berkeley, independently reported highly sensitive transistors made from metallic carbon nanotubes. These devices could be turned on and off by a

THE AUTHOR

CHARLES M. LIEBER spent much of his childhood building—and breaking—stereos, cars and model airplanes. He is now the Mark Hyman Professor of Chemistry at Harvard University, where he directs a group of 25 undergraduate, graduate and postdoctoral researchers who focus on nanoscale science and technology. Lieber recently founded NanoSys, Inc., with Larry Bock of CW Ventures and Hongkun Park of Harvard. Their modest goal: to revolutionize chemical and biological sensing, electronics, optoelectronics, and information storage.

single electron but required very low temperatures to operate. This past July Dekker's team swept away this limitation. The researchers used an atomic force microscope to create a singleelectron transistor that could function at room temperature. Dekker and his co-workers have also fashioned a more conventional field-effect transistor, the building block of most integrated circuits today, out of a carbon nanotube, and McEuen's group has combined metallic and semiconductor nanotubes into

a diode, which allows electric current to pass in one direction only. Finally, my group has demonstrated a very different type of switch, a nanoscale electromechanical relay.

Hot Wire

A MAJOR PROBLEM with nanotubes is that they are difficult to make uniform. Because a slight variation in diameter can spell the difference between a conductor and a semiconductor,

DNA Computing

WHY LIMIT OURSELVES TO ELECTRONICS? Most efforts to shrink computers assume that these machines will continue to operate much as they do today, using electrons to carry information and transistors to process it. Yet a nanoscale computer could operate by completely different means. One of the most exciting possibilities is to exploit the carrier of genetic information in living organisms, DNA.

The molecule of life can store vast quantities of data in its sequence of four bases (adenine, thymine, guanine and cytosine), and natural enzymes can manipulate this information in a highly parallel manner. The power of this approach was first brought to light by 🕠 computer scientist Leonard M. Adleman in 1994. He showed that a DNA-based computer could solve a tupe of problem that is particularly difficult for ordinary computers—the Hamiltonian path problem, which is related to the infamous traveling-salesman problem [see "Computing with DNA," by Leonard M. Adleman; SCIENTIFIC AMERICAN, August 1998].

Adleman started by creating a chemical solution of DNA. The individual DNA molecules encoded every possible pathway between two points. By going through a series of separation and amplification steps, Adleman weeded out the wrong paths-those, for example, that contained points they were not supposed to contain—until he had isolated the right one. More recently, Lloyd M. Smith's group at the University of Wisconsin-Madison implemented a similar algorithm using gene chips, which may lend themselves better to practical computing (diagram).

Despite the advantages of DNA computing for otherwise intractable problems, many challenges remain, including the high incidence of errors caused by base-pair mismatches and the huge number of DNA nanoelements needed for even a modest computation. DNA computing may ultimately merge with other types of nanoelectronics, taking advantage of the integration and sensing made possible by nanowires and nanotubes. -C.M.L.



Single DNA strands are attached to a silicon chip. They encode all possible values of the variables in an equation that the researchers want to solve.



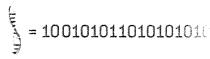
Copies of a complementary strand—which encodes the first clause of the equation—are poured onto the chip. These copies attach themselves to any strand that represents a valid solution of the clause. Any invalid solutions remain a single strand.



An enzyme removes all the single strands.



Other processes melt away the added complementary strands. These steps are repeated with all the clauses of the equation.



The DNA strand that survives this whole process represents the solution to the whole equation.

BRYAN CHRISTIE

Soon nanodevices may have useful applications—for example, as **ultrasensitive detectors** of gas molecules and biological compounds.

a large batch of nanotubes may contain only a few working devices. In April of this year Phaedon Avouris and his colleagues at the IBM Thomas J. Watson Research Center came up with a solution. They started with a mixture of conducting and semiconducting nanotubes and, by applying a current between metal electrodes, selectively burned away the conducting ones until just semiconducting ones were left. The solution is only partial, however, because it requires the use of conventional lithography to wire up the random nanotube array and then test and modify each of the individual elements, which would ultimately number in the billions.

My group has also been working on a different type of nanoscale wire, which we term the semiconductor nanowire. It is about the same size as a carbon nanotube, but its composition is easier to control precisely. To synthesize these wires, we start with a metal catalyst, which defines the diameter of the growing wire and serves as the site where molecules of the desired material tend to collect. As the nanowires grow, we incorporate chemical dopants (impurities that add or remove electrons), thereby controlling whether the nanowires are *n*-type (having extra electrons) or *p*-type (having a shortage of electrons or, equivalently, a surfeit of positively charged "holes").

The availability of *n*- and *p*-type materials, which are the essential ingredients of transistors, diodes and other electronic devices, has opened up a new world for us. We have assembled a wide range of devices, including both major types of transistors (field-effect and bipolar); inverters, which transform a "0" signal to a "1"; and light-emitting diodes, which pave the way for optical interconnections. Our bipolar transistors were the first molecular-scale devices ever to amplify a current. A recent advance in my lab by Xiangfeng Duan has been the assembly of memory from crisscrossing *n*- and *p*-type nanowires. The memory can store information for 10 minutes or longer by trapping charge at the interface between the crossing nanowires [see illustration on next page].

Breaking the Logjam

BUILDING UP AN ARSENAL of molecular and nanoscale devices is just the first step. Interconnecting and integrating these devices is perhaps the much greater challenge. First, the nanodevices must be connected to molecular-scale wires. To date, organic-molecule devices have been hooked up to conventional metal wires created by lithography. It will not be easy to substitute nanowires, because we do not know how to make a good electrical connection without ruining these tiny wires in the process. Using nanowires and nanotubes both for the devices and for the interconnections would solve that problem.

Second, once the components are attached to nanowires, the

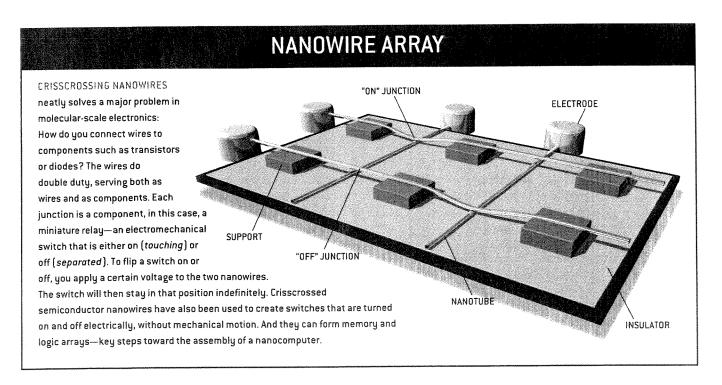
wires themselves must be organized into, for example, a twodimensional array. In a report published earlier this year, Duan and another member of my team, Yu Huang, made a very significant breakthrough: they assembled nanocircuits by means of fluid flows. Just as sticks and logs can flow down a river, nanoscale wires can be drawn into parallel lines using fluids. In my lab we have used ethanol and other solutions and controlled the liquid flow by passing it through channels molded into polymer blocks, which can be easily placed on the substrate where we wish to assemble devices.

The process creates interconnections in the direction of the fluid flow: if the flow is along only one channel, then parallel nanowires are formed. To add wires in other directions, we redirect the flow and repeat the process, building up additional layers of nanowires. For instance, to produce a right-angle grid, we first lay down a series of parallel nanowires, then rotate the direction of flow by 90 degrees and lay down another series. By using wires of different compositions for each layer, we can rapidly assemble an array of functional nanodevices using equipment not much more sophisticated than a high school chemistry lab. A grid of diodes, for example, consists of a layer of conducting nanotubes above a layer of semiconductor nanotubes, or a layer of *n*-type nanowires atop a layer of *p*-type nanowires. In both cases, each junction serves as a diode.

Our approach, which is similar to that being pursued by the team at U.C.L.A. and Hewlett-Packard, is deterministic. We are trying to create arrays with a certain predictable behavior. Form follows function. An alternative proposed by the group at Rice, Yale and Penn State is to allow blocks of devices and wires to interconnect at random. Later, the ensemble can be analyzed to determine how it might be used for storage or computation. In this case, function follows form. The problem with this procedure is that it would take a huge effort to map a complex network and figure out what use it could be put to.

Intimately linked to all these efforts is the development of architectures that best exploit the unique features of nanoscale devices and the capabilities of bottom-up assembly. Although we can make unfathomable numbers of dirt-cheap nanostructures, the devices are much less reliable than their microelectronic counterparts, and our capacity for assembly and organization is still quite primitive.

In collaboration with André DeHon of the California Institute of Technology, my group has been working on highly simplified architectures that can be generalized for universal computing machines. For memory, the architecture starts with a two-dimensional array of crossed nanowires or suspended electromechanical switches in which one can store information at each cross point. The same basic architecture is being pur-



sued by researchers at U.C.L.A. and Hewlett-Packard, and it resembles the magnetic-core memory that was common in computers of the 1950s and 1960s.

Law of Large Numbers

TO OVERCOME the unreliability of individual nanodevices, we may rely on sheer numbers—the gizmos are so cheap that plenty of spares are always available. Researchers who work on defect tolerance have shown that computing is possible even if many of the components fail, although identifying and mapping the defects can be slow and time-consuming. Ultimately we hope to partition the enormous arrays into subarrays whose reliability can be easily monitored. The optimum size of these subarrays will depend on the defect levels typically present in molecular and nanoscale devices.

Another significant hurdle faced by nanoelectronics is "bootstrapping." How do engineers get the circuit to do what they want it to? In microelectronics, circuit designers work like architects: they prepare a blueprint of a circuit, and a fabrication plant builds it. In nanoelectronics, designers will have to work like computer programmers. A fabrication plant will create a raw nanocircuit—billions on billions of devices and wires whose functioning is rather limited. From the outside, it will look like a lump of material with a handful of wires sticking out. Using those few wires, engineers will somehow have to configure those billions of devices. Challenges such as this are what keeps me tremendously excited about the field as a whole.

Even before we solve these problems, nanodevices may have useful applications. For example, semiconducting carbon nanotubes have been used by Hongjie Dai's group at Stanford University to detect gas molecules, and Yi Cui in my group has used semiconductor nanowires as ultrasensitive detectors for a wide

range of biological compounds. In our work at Harvard, we have converted nanowire field-effect transistors into sensors by modifying their surfaces with molecular receptors. This technology has the potential of detecting single molecules using only a voltmeter from a hardware store. The small size and sensitivity of nanowires also make possible the assembly of extremely powerful sensors that could, for instance, sequence the entire human genome on a single chip and serve in minimally invasive medical devices. In the nearer term, we could see hybrids of micro and nano: silicon with a nano core—perhaps a high-density computer memory that retains its contents forever.

Although substantial work remains before nanoelectronics makes its way into computers, this goal now seems less hazy than it was even a year ago. As we gain confidence, we will learn not just to shrink digital microelectronics but also to go where no digital circuit has gone before. Nanoscale devices that exhibit quantum phenomena, for example, could be exploited in quantum encryption and quantum computing. The richness of the nanoworld will change the macroworld.

MORE TO EXPLORE

The author's Web site: cmliris.harvard.edu

The Avouris group: www.research.ibm.com/nanoscience

The Dai group: www-chem.stanford.edu/group/dai

The DeHon group: www.cs.caltech.edu/~andre

The Dekker group: www.mb.tn.tudelft.nl/user/dekker

The McEuen group:

www.lassp.cornell.edu/lassp.data/mceuen/homepage/welcome.html

The Penn State team: stm1.chem.psu.edu

The Rice/Yale team: www.imtour.com and www.eng.yale.edu/reedlab

The Smith group: www.chem.wisc.edu/~smith

The U.C.L.A./Hewlett-Packard team: www.chem.ucla.edu/~schung/hgrp and www.hpl.hp.com/research/qsr/staff/kuekes.html