As conventional silicon chips race toward their physical limits, researchers are seeking the Next Small Thing in electronics through chemistry

Assembling Nanocircuits From the Bottom Up

NANOCOMPUTING

Microelectronics has an impressive record of packing ever more transistors on computer chips. This special focus section looks at new ways researchers are attempting to keep those gains coming and some hurdles they face in doing so.

▶ MOLECULAR ELECTRONICS

EUV LITHOGRAPHY

LIMITS TO GROWTH

LOS ANGELES, CALIFORNIA—Nothing says "high tech" like the sight of computer-chip engineers padding around a yellow-tinted clean room covered head to toe in jumpsuits resembling surgical scrubs. James Heath's chemistry lab on the third floor of the University of California, Los Angeles's (UCLA's) geology building has none of those trappings; just a few grad students and postdocs wearing the usual academic uniform of T-shirts and jeans, hunched over blacktopped lab benches. Intel territory this is not—at least, not yet.

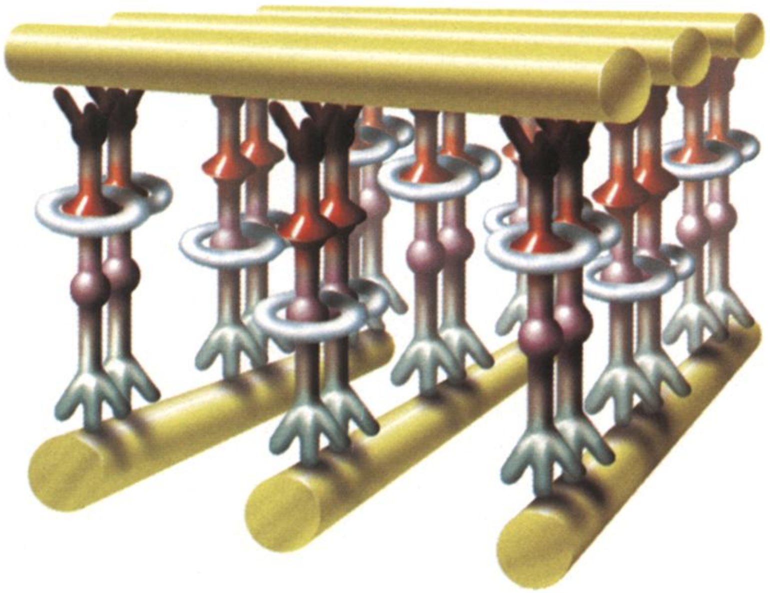
In a 10-centimeter glass dish atop one of these benches, some of the smallest computer circuitry ever dreamed of is in the making. The setting may not look impressive, but what's happening here may provide a glimpse of the future for the multibillion-dollar microelectronics industry.

Mike Diehl, one of Heath's graduate students, pulls back a piece of crinkled aluminum foil from atop the dish to reveal four wedge-shaped portions of a silvery silicon wafer in a bath of clear organic solvent. On each wedge are two gold squares connected by a stair step–shaped wire. What's not visible, says Diehl, is that the step portion of the wire is actually two parallel wires close together. Spanning the gap between them are carbon nanotubes, each a three-dimensional straw of carbon atoms about 1 nanometer across and perhaps a micrometer long. Using electrical voltages applied between the pairs of invisible wires and a separate step involving moving fluids, Diehl and others in the Heath lab have come up with methods to array these nanotubes in perpendicular rows, one atop another in a crossbar arrangement. When an electrical current is applied to a nanotube in one row, it can pass that current to intersecting nanotubes. Next, Heath's group plans to put a layer of organic molecules between the nanotubes that will act as transistorlike switches. If all goes well, within weeks they'll have arrays of some of the smallest circuits ever produced.

Crossbars are simple stuff compared with the intricate patterns on everyday semiconductor chips. What's impressive is the scale. By making devices from small groups of molecules, researchers may be able to pack computer chips with billions of transistors, more than 30 times as many as current technology can achieve. That could open the door to fanciful computing applications such as computers that recognize and respond to everyday speech and translate conversations on the fly. And it's all happening with just the beakers, solvents, and fluid flow chambers of benchtop chemistry.

Heath and a growing cadre of chemists, materials scientists, and physicists are pursuing molecular electronics: the attempt to use chemistry to build circuits from the bottom up instead of carving bigger pieces of matter into smaller and smaller chunks, as chip manufacturers now do. The idea has long had critics and detractors, who say the approach will never achieve the reliability and performance chipmakers demand. But as the field begins to grow in sophistication, it's starting to earn new respect. In the past few years, researchers have fashioned an impressive array of chiplike devices from handfuls of individual molecules. Now they are beginning to take the next key step, linking those individual components into more complex circuits such as the Heath group's crossbars.

Within just the last 2 years, "the progress has been pretty mind-boggling," says William Warren, who heads the molecular electronics initiative at the Defense Advanced Research Projects Agency, which sponsors molecular electronics research at labs around the United States. Adds chemist Tom Mallouk of Pennsylvania State University, University Park: "People are publishing really interesting stuff that has the potential to change the field at a very heady clip."



Molecular memory circuit. In a promising array design, currents passed between perpendicular nanowires alter the conductivity of organic molecules sandwiched in between.

ILLUSTRATION: C. SLAYDEN

Breaking the law

Silicon-based electronics has been moving along at a steady clip itself. For the past 35 years, chipmakers have managed to double the number of transistors on computer chips every 18 months by shrinking their size, a trend known as Moore's Law after Intel cofounder Gordon Moore, who noted the trend in 1965. Today, chip engi-

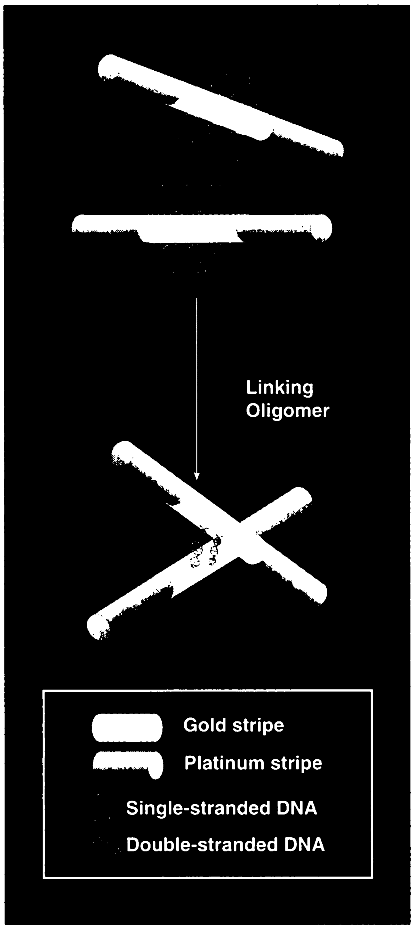
Yet Another Role for DNA?

As they struggle to join nanotubes and nanowires into simple X shapes, molecular electronics researchers dream of making much more complex circuitry. "Everybody is trying to make larger arrays" of devices, says Tom Mallouk, a chemist at Pennsylvania State University, University Park. "What we're seeing now is just the beginning." To move from the simple to the complex, though, scientists will need to develop a much defter touch.

Some think the key to that dexterity lies in that consummate molecular sleight-of-hand artist, DNA. By taking advantage of DNA's ability to recognize molecules and self-assemble—not to mention the huge toolkit of enzymes and techniques biologists have developed for working with the molecule—they hope to use DNA as a template for crafting metallic wiring, or even to wire circuits with strands of DNA itself.

Mallouk's group, also led by chemist Christine Keating and electrical engineers Tom Jackson and Theresa Mayer, starts by growing metal nanowires in the tiny pores of commercially available filtration membranes. Because the researchers can vary the composition of the metals laid down in the pores, they make nanowires with one type of metal, such as platinum, on the ends, and another metal, such as gold, in the middle. By attaching gold-linking thiol groups to single-stranded DNA, they can bind the DNA to the gold midsections of the nanowire. To coax the nanowires to assemble into different shapes, they simply attach complementary DNA strands to the gold segments of other nanowires. The complementary strands then bind to each other, welding pairs of wires together.

In initial experiments, the team has used the technique to make simple shapes such as crosses and triangles. And they are currently using it in an attempt to assemble more complex circuitry, Keating says: "You can envision using this to carry out the deterministic assembly of a circuit." That hasn't happened yet, in part because the DNA on some nanowires tends to bind indiscriminately to other noncomplementary DNA rather than its partner strand. But because biochemists have learned to solve this problem with applications such as DNA chips, Keating is confident that DNA will soon become a type of addressable glue for a wide variety of molecular electronics components.



Matchmaker. A piece of single-stranded DNA links corresponding sequences on nanowires to forge a cross.

Erez Braun and his group at the Technion–Israel Institute of Technology in Haifa take a different approach. Instead of using DNA to join wires together, they make wires by silver-plating DNA itself (*Science*, 20 March 1998, p. 1967). The researchers start with a pair of gold electrodes 1200 nanometers apart on a sheet of glass. First they attach snippets of DNA 12 oligonucleotides long to each electrode. Then they immerse the electrodes in a solution containing short lengths of viral DNA. The viral DNA attaches itself to the snippets, creating a DNA bridge between the electrodes. Next, by soaking the bridge in a solution containing silver ions, Braun and colleagues coat it with silver. The result is a nanometer-scale metallic wire between the electrodes, with properties that can be varied by fiddling with the developing conditions.

Braun says they have extended the approach and are now close to completing a three-terminal switching device that would function much like a transistor. They are also studying how they might scale up these processes to create more complex networks.

More exotically, it's even possible that wires might be made of DNA itself. First, though, researchers will need a much better understanding of DNA's basic electrical properties. Since the first report, in 1993, that DNA can carry current, measurements of its conductivity have ranged from zero, a perfect insulator, to superconductivity when the electrodes are spaced very closely together. Christian Schönenberger, a physicist at the Swiss Nanoscience Center in Basel, says most researchers now think that DNA is a semiconductor whose conductivity depends on how it is "doped" with foreign molecules. The wide range of conductivity is good news, Schönenberger says. "It means that we can, in principle, tailor the doping and control the conductivity." To make electronic devices, though, scientists must sort out precisely which parts of DNA's complex chemistry do the doping—and that may be no simple task. **–D.N. AND R.F.S.**

neers can make features close to 100 nanometers across, and they're already eyeing a version of the technology that could cut that in half (see p. 787).

Molecular electronics has the potential to go much smaller, with components composed of just tens or hundreds of molecules. That would clearly accelerate the march of Moore's Law. But it could do much more as well. For one, it might solve a problem that is already beginning to vex chipmakers: heat. Wires carved into silicon by the standard technique of lithography are riddled with imperfections along their edges. As wires shrink, electrons coursing through them run an ever greater chance of smashing into one of these defects and generating unwanted heat. Pack too many circuits onto a chip and you get burnout. Lacking such imperfections, molecules such as nanotubes are expected to do a better job of preventing electrical losses as well as containing electrons that travel along their lengths.

Perhaps most important, a shift from silicon to molecules could also break Moore's Second Law, a corollary to the first, which states that the cost of new chip-fabrication plants increases exponentially as the features get smaller. By 2015, experts suggest, they will cost somewhere between \$50 billion and \$200 billion apiece. Because molecular electronics relies on molecules to assemble themselves rather than on lithography, self-assembly "is likely to beat [Moore's Second Law] before it beats the first," says Mallouk. Adds Mark Ratner, a chemist at Northwestern University in Evanston, Illinois, and one of the fathers of the field: "It's cheap to make molecules. It's expensive to make fabs."

ILLUSTRATION: J. MOGLIA

Small-time start

The idea of wiring small numbers of molecules into logic and memory devices has been around almost as long as the silicon chips they may one day replace. Ratner and IBM's Ari Aviram first suggested making molecular-scale electronic devices back in 1974. But at the time it was a pipe dream, because key techniques weren't available. That began to change in the mid-1980s with the invention of scanning probe microscopes, which enabled researchers to see individual atoms on surfaces and arrange them at will.

The advance prompted Jim Tour of Rice University in Houston and other chemists to take up the challenge anew in the early 1990s. They designed organic molecules that they calculated could either store electrons, like a tiny memory device, or alter their conductivity much as a transistor controls the ability of an electrical current to flow between two electrodes.

But turning those molecules into working molecular-scale devices was no simple matter. "Nanoelectronics are a physicist's dream but an engineer's nightmare," says Warren. The tide finally began to turn in July 1999 when Heath, UCLA's J. Fraser Stoddart, and collaborators at Hewlett-Packard Corp. (HP) published a paper describing a molecular fuse that, when hit with the right voltage, altered the shape of molecules trapped at a junction between two wires (*Science*, 16 July 1999, p. 391). The change destroyed the molecules' ability to carry current across the junction. For this initial demonstration, the UCLA-HP team used lithography to make crossbars. They also wired several switches together to perform rudimentary logic operations. The devices worked well, but they had a big drawback: Once they flipped to the off position, they couldn't be turned back on again.

Within months, Tour, Yale University's Mark Reed, and their colleagues published a separate approach to make a device that could switch current on and off like a transistor. And last year, the UCLA-HP group fired back with an improved organic compound pinned at the junction between two wires that could also be switched (*Science*, 18 August 2000, p. 1172).

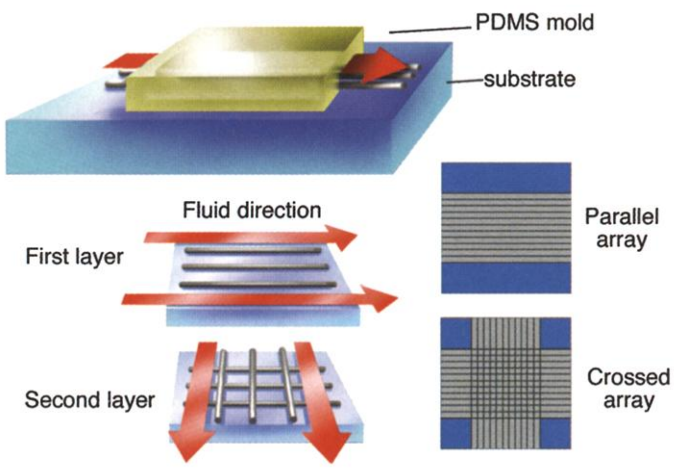
Meanwhile, related work on very different devices was progressing on a separate track: Several teams were making more or less conventional transistors sporting a few nanoscale components. In 1998, for example, physicist Cees Dekker of Delft University in the Netherlands reported using semiconducting nanotubes as the key charge-conducting layer, called the channel, in transistors.

Dekker's original nanotube transistors marked a breakthrough in the use of nanotubes in working electrical devices, but they performed poorly. One reason was the poor electrical contact between the nanotubes and the electrodes to which they were connected. At the March American Physical Society (APS) meeting in Seattle, however, Phaedon Avouris and his colleagues at IBM's T. J. Watson Research Center in Yorktown Heights, New York, reported solving this problem with a technique for welding the ends of nanotubes to the metal electrodes on either end of a transistor's channel. That gave individual nanotubes performance rivaling that of conventional silicon transistors. They also devised a way to chemically alter the nanotubes so they could conduct both negatively charged electrons and positive charges called holes, which are essentially the absence of electrons in a material. That feat enables them to make both "n-type" devices that conduct electrons and "p-type" devices that transport positively charged holes. In today's chips, combinations of n- and p-type transistors form the building blocks for complex circuits.

Putting it together

Avouris's team at IBM has already started making such circuits with nanotube transistors. At the APS meeting, Avouris described how he and his colleagues combined chemistry and conventional lithography to pattern a pair of transistors into a simple device called an inverter, a basic component of more complex circuitry. They also constructed an array of nanotube transistors, although they have yet to wire them together to carry out specialized logic or memory functions.

Like the IBM team, several others are shrinking some components down to the molecular scale, while leaving other portions larger and thus easier to wire together and to the outside world. In April, Heath's group reported a key success with this hybrid approach. At the American Chemical Society meeting in San Diego, Heath reported having made a 16-bit memory cell. The cell, the most complex of its kind to date, used the same crossbar arrangement of nanowires that Diehl is perfecting with nanotubes. The nanowires were made by e-beam lithography, a high-resolution patterning technique that is painfully slow and thus impractical for large-scale manufacturing. Nevertheless, Heath is excited about his team's early success. "It's the first nanocircuit that works," he says. And within a year and a half, Heath expects that his lab will complete the first molecular electronic–based integrated circuit complete with logic elements and memory circuits that can talk to one another in computer-friendly 0's and 1's.



Pouring it on. Charles Lieber's team aligns stacks of nanowires with liquid streaming through a mold.

Heath will have competition for that prize. Another group in the hunt is led by Harvard University chemist Charles Lieber. In a trio of papers published earlier this year in *Science* and *Nature*, Lieber's team reported making nanowires out of a variety of semiconductors, which they could then arrange into either individual devices or more complex crossbar arrays.

Lieber contends that semiconductor nanowires are better building blocks for molecular electronics than carbon nanotubes are, as their electronic properties can be more precisely controlled. Although nanotubes can conduct like either metals or semiconductors, depending on their geometry, there is no way yet to synthesize a pure batch of one type or the other. That makes it hard to get the same performance from each device, Lieber says. By contrast, the electronic properties of semiconductor nanowires can be precisely controlled by adding trace amounts of "dopant" elements during synthesis. This "doping" is a key feature of today's semiconductor chips, because it allows engineers to make both n-type and p-type devices, and the same holds true on the nanoscale, says Lieber.

In the 4 January issue of *Nature*, Lieber's team reported having wired n-type and p-type indium phosphide nanowires into nanosized field-effect transistors, the devices at the heart of today's microelectronics. And in the 2 February issue of *Science* (p. 851), the team described related devices made from n-type and p-type silicon, the mainstay material of today's semiconductor industry.

Lieber and colleagues showed that they could up the level of complexity as well. In

ILLUSTRATION: C. SLAYDEN

the 26 January issue of *Science* (p. 630), they reported using a combination of prepatterned lines of adhesive compound and moving fluids to arrange nanowires in parallel arrays, triangles, and crossbars, resembling the crossbars made by Heath's group. To make the crossbars, the team started by crafting a flat, rubbery mold prepatterned with tiny parallel channels. They placed this mold atop a silicon substrate and flowed a suspension of nanowires in an ethanol solution through the channels, aligning one layer of nanowires in the same orientation. They then turned their mold 90 degrees and repeated the procedure, depositing another row of parallel nanowires atop the first. (See figure, p. 784.)

To show that the arrays were electrically active, Lieber's team made a 2 × 2 crossbar that resembled a tic-tac-toe board. They then used e-beam lithography to place tiny electrical contacts to the outside world at each end of the four wires in the array. By applying voltages between the various pads, they showed that they could produce transistor-like performance at any of the four junctions they chose. "Using solution phase, bottom-up assembly, we can make functional devices," says Lieber.

A hybrid future?

Crossbars and nanotubes may be fine for basic research. But many researchers doubt whether they will ever produce circuitry that can run Quake, surf the Web, or even handle a simple word processor. Early on, researchers in the field "made all kinds of crazy promises," says Edwin Chandross, a materials chemist at Bell Laboratories, the research arm of Lucent Technologies in Murray Hill, New Jersey. In particular, says Chandross, molecular electronics researchers pushed the notion that engineers would make computing devices out of single molecules. That's nonsense, he says, because a single unruly molecule could disrupt a device and thus corrupt the larger system. Today, Chandross is pleased by what he sees as a more realistic approach of using ensembles of molecules to work together in individual devices. Still, "it's a real long way off from being practical," says Rick Lytel, a physicist at Sun Microsystems in Palo Alto, California. Sunlin Chou, who helps direct Intel's work on advanced circuitry, agrees: "It's very blue sky."

"Gee, the vacuum tube guys said that too" about semiconductor electronics, says Heath, undaunted. "If we can make a nano–integrated circuit and interface it to lithography, you've got to argue that's pretty interesting," he says. "I want to know how far we can go."

Heath, Mallouk, and many others expect that even increasingly sophisticated molecular-electronics devices are unlikely to make it into the computing world on their own. Rather, they will form a hybrid technology that combines self-assembling molecular electronics components with traditional silicon electronics made by lithography. "I think the most likely approach will use lithography to get down to submicrometer dimensions and then self-assemble the little pieces inside," says Mallouk.

Even in the established world of silicon electronics, that vision is opening eyes. In addition to Hewlett-Packard, companies including IBM and Motorola are starting to pump research dollars into the area. So are start-ups such as Molecular Electronics Corp. of State College, Pennsylvania. "A number of companies are looking at this, because none of them want to be in a position of not being up on the technology if and when the breakthroughs come," Mallouk says.

Those breakthroughs may or may not ultimately make circuitry smaller than high-tech silicon fabs can achieve today. But if molecular-electronics researchers can teach circuits to assemble themselves, that trick will give them a cost advantage that no chipmakers will be able to ignore.

–ROBERT F. SERVICE

NANOCOMPUTING

▶ EUV LITHOGRAPHY

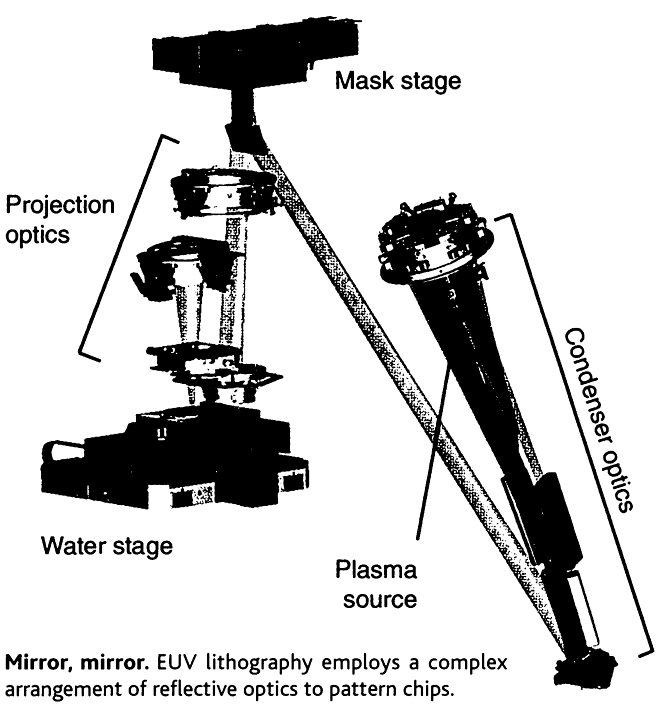
Optical Lithography Goes To Extremes—And Beyond

In search of ever finer detail, chipmakers are pushing conventional printing techniques toward the physical limits of light

LIVERMORE, CALIFORNIA—The speed of light sets an upper limit for those dabbling in relativity, but makers of computer chips are concerned with another of light's limiting properties: its wavelength. Current chipmaking technologies may soon bump up against that limit, say proponents of molecular electronics and other futuristic computing schemes, and that will confound the semiconductor industry's ability to shrink transistors and other devices. Craig Barrett, CEO of the world's largest chipmaker Intel, begs to differ.

In April, Barrett and other leaders of a chip-patterning research consortium gathered here to unveil a first-of-its-kind machine that uses extreme ultraviolet light to print features on chips. The new machine has already created features as small as 80 nanometers across on silicon wafers, a resolution that is expected to boost the speed of integrated circuits from 1.5 gigahertz today to 10 gigahertz in 2005–06. Ultimately, Barrett and others argue, the technology will be able to turn out features as small as 10 nanometers, nearly the same scale as molecular electronic devices.

The triumph makes the technique, known as extreme ultraviolet (EUV) lithography, "one of the leading horses in the race" to succeed today's optical lithography for carving ever smaller features into silicon, Barrett says. Today, conventional lithography patterns chips by shining ultraviolet light through a stencil with slits in the shape of features to be transferred onto a chip. Lenses below the stencil then reduce that pattern to one-quarter its original size and project it onto a region of a silicon wafer coated with a polymer known as a resist. The light transforms the resist so that chemical etchants can eat away either the region hit with the light or the shaded region. Engineers can then carve away part of the silicon wafer below and fill the



Mirror, mirror. EUV lithography employs a complex arrangement of reflective optics to pattern chips.

CREDIT: SCIENCE AND TECHNOLOGY REVIEW, LLNL