

Organic semiconductor devices can make more than just bendable displays.

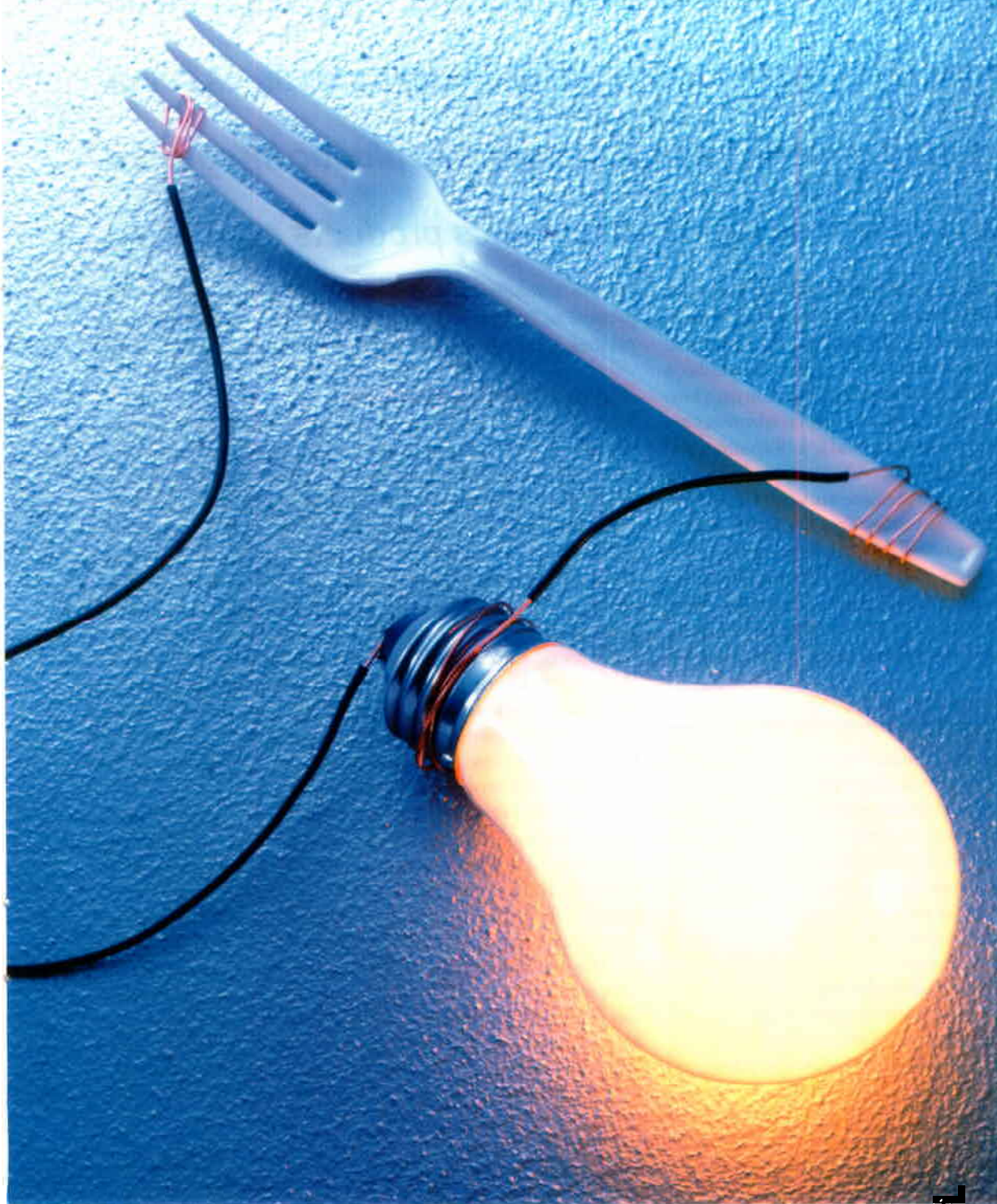
They will find use in wearable electronics, chemical sensors, skin for robots and innumerable other applications

Next Stretch for **PLASTIC**



ELECTRONICS

By Graham P. Collins



Strong, flexible, lightweight and cheap, plastics have acquired an additional attribute in recent years: the ability to function as semiconductors, forming diodes and transistors in plastic integrated circuits. Now, as the first plastic electronics products are hitting

the market in displays that use organic light-emitting diodes, the stage is set for a new era of pervasive computing with polymers. Plastics may never match the sheer processing speed and miniaturization of silicon, but they will be able to go places that silicon cannot reach: ultracheap radio-frequency identification tags; low-end, high-volume data storage; displays that are inexpensive, even disposable, or that can be wrapped around a wall column; and wearable computing. Other uses for conductive plastics include photocells, chemical sensors and pressure-sensitive materials.

A key advantage of organic transistors over silicon is their ease of fabrication. Building a state-of-the-art silicon chip takes weeks of work using complex and expensive processes such as photolithography and vacuum deposition, carried out under high temperatures in ultraclean rooms. In comparison, organic transistors can be made using faster, cheaper processes un-

der less carefully controlled conditions. Finally, there is the promise of “roll-to-roll” fabrication similar to the continuous printing presses that revolutionized publishing.

Organic Semiconductors

THE CONDUCTIVE PLASTICS in electronics come in two broad types. One is made out of small organic molecules, the other out of long, conjugated polymer molecules. An example of the small-molecule variant is pentacene, which consists of five benzene rings joined in a line [see box on page 78]. The long polymers consist of chains of hundreds or thousands of carbon atoms. “Conjugated” means that the carbon atoms in the chains are joined by alternating double and single bonds. A benzene ring can also be thought of as a short chain of six such carbon atoms, with alternating bonds, biting its tail to form a closed loop. But that picture of alternating single and double bonds is not the most accurate way of viewing any of these molecules. Instead some of the double-bond electrons become delocalized, shared among several atoms rather than localized in a specific bond between two atoms.

Such delocalization is similar to what happens in metals and semiconductors. The delocalized electrons can exist only in states that have specific energy levels. The permitted energies form bands that can hold only so many electrons [see box on page 78]. The highest-energy band containing electrons is called the valence band, and the next higher one is the conduction band.

The small molecules, such as pentacene, are conductive in their pure state, and they can be made directly into crystals or thin films for use in devices. The long polymers, in contrast, are generally poor conductors in their pure state. The reason is that their valence band is full of electrons, which obstructs current flow. Each electron in the band has nowhere to go—it has no

Overview/*Plastic Electronics*

- Plastics have long formed the skeletons and skin of products, whereas silicon has supplied the brains. With the advent of polymer and crystalline organic electronics, plastics will make up the brains as well as the brawn.
- Plastic chips may never be as fast or as miniaturized as silicon chips, but their production by convenient techniques, including ink-jet printing, promises extremely cheap devices that could become ubiquitous in consumer products and household appliances.
- Potential uses include information displays for appliances and computers, electronic paper, radio-frequency identification tags, wearable electronics, chemical sensors and pressure-sensitive skin for robots.

empty states available where it can move. The empty spaces in the conduction band are at too high an energy level to be of use.

To change that situation, researchers introduce special impurity atoms (called doping). The dopant atoms either add extra electrons, which go into the conduction band, or they remove some electrons from the valence band, creating holes, which behave like positive particles. In either case, current can flow easily, either by conduction electrons traveling along in the almost empty conduction band or by holes traveling through the valence band. (From the perspective of a hole, the valence band is almost empty: every electron there is akin to a location to which the hole can move.)

The possibility of doping conjugated polymers in this way to create a conducting or semiconducting material was discovered in the 1970s by Alan J. Heeger (now at the University of California at Santa Barbara), Alan G. MacDiarmid (now at the University of Pennsylvania), Hideki Shirakawa (now at the University of Tsukuba in Japan) and their co-workers. Heeger, MacDiarmid and Shirakawa received the 2000 Nobel Prize in Chemistry for this work. They doped polyacetylene by exposing it in various experiments to chlorine, bromine or iodine.

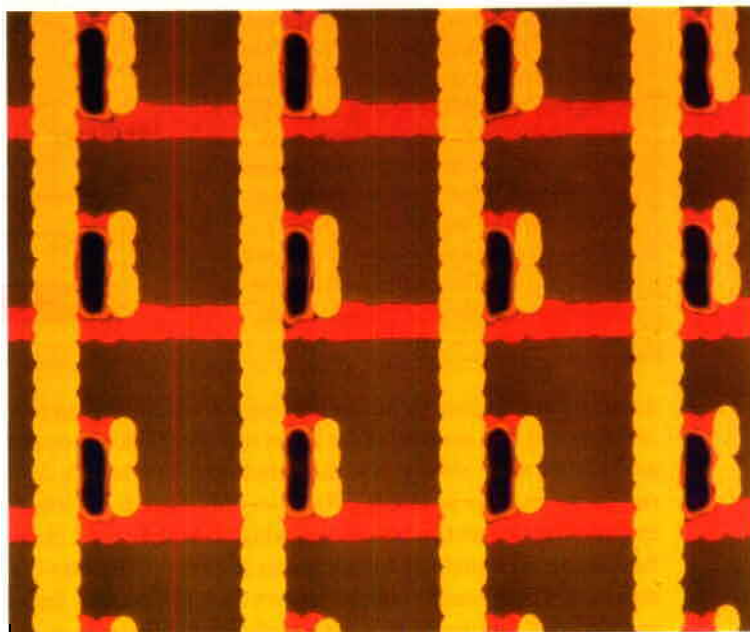
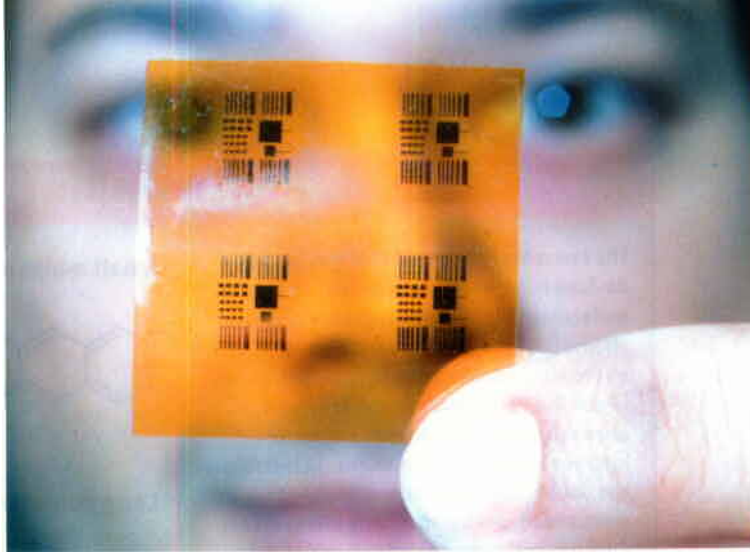
These conductive plastics have already found a number of applications other than electronic circuitry, including use as a corrosion inhibitor, electromagnetic shielding for electronic circuits, an antistatic coating on photographic emulsions, and a microwave-absorbing stealth coating to hide an object from radar.

Printing Machines

THE SMALL-MOLECULE organic semiconductors are best fabricated into devices by vapor deposition: the compound is vaporized in a closed chamber, either evacuated or filled with an inert gas, and allowed to condense in a film onto a substrate. This technique is similar to that used in the manufacture of some very quotidian products, such as the coating on potato chip bags that prevents oxygen from diffusing through the plastic.

Polymers offer a number of fabrication techniques. One is spin-coating, in which a disk with a blob of a solution containing the polymer or its precursors is spun, spreading the material evenly across the disk. The material can then be etched by photolithographic techniques similar to those used in making conventional inorganic semiconductors or cut or imprinted in other ways. (Some researchers have also used spin-coating with pentacene.)

One problem with conductive polymers compared with the plastics used in other industries is their lack of solubility in convenient organic solvents. For example, polyethylenedioxythiophene, or PEDOT, is typically laid down in an acidic water-based solution whose corrosive properties cause other problems. In April, TDA Research in Wheat Ridge, Colo., announced a new form of PEDOT dubbed oligotron, which is soluble in noncorrosive organic solvents. Shining ultraviolet (UV) light on the liquid precursor causes its molecules to cross-link, curing the material into an insoluble solid. Thus, it should be possible to spin-coat oligotron and then make a pattern by shining UV light on it through a mask.



PLASTIC TRANSISTOR ARRAYS were patterned using ink-jet printing by the Palo Alto Research Center (PARC). The lower image shows 12 transistors of an array. The dots are about 40 microns in diameter. The researchers used a semiconducting polymer ink developed by Beng Ong of the Xerox Research Center of Canada. The transistors would be suitable for use in active-matrix displays, electronic paper and other applications.

Alternatively, it could be ink-jet-printed in a pattern and then fixed with UV radiation. The ink-jet process is highly analogous to graphical ink-jet printing, but instead of colored dyes, tiny droplets of polymer solution are propelled onto the substrate in carefully controlled patterns. So far only a large-scale proof-of-principle pattern has been demonstrated; no electronic devices have been made.

The trick to making oligotron soluble was to attach appropriate groups on the end of the PEDOT monomer molecules. It should be possible to create variants of oligotron with specific properties by modifying the end groups. For instance, oligotron with photovoltaic end groups might be used to make solar cells.

Several companies are pursuing the ink-jet technique of circuitry printing. The Palo Alto Research Center (PARC, formerly a part of Xerox) has demonstrated such technology; in 2003 its researchers produced the first plastic semiconductor transis-

CONDUCTIVE PLASTICS

The raw materials for organic electronic devices come in two broad classes: small molecules [top] and conjugated polymer chains [middle], both of which have alternating double and single carbon bonds. (Each line in these diagrams is a bond between two carbon atoms. Bonds to hydrogen atoms are not shown.) Electrons in the double bonds become somewhat delocalized, or shared among many atoms. Consequently, the allowed states of the electrons form bands over ranges of energy [bottom]. The electrical properties of the material depend on the separation and the filling of the bands. Generally, the polymers have a full valence band, making them insulating. When dopant chemicals [such as sodium] are added, however, electrons contributed to the conduction band or removed from the valence band enable a current to flow. The small molecules are semiconducting in their undoped state.

Small molecule (pentacene)



Pentacene showing delocalized electrons



Shared bond electrons

Long polymer (polyacetylene)



Chain continues

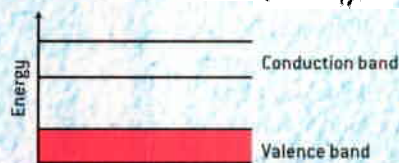
Doped polymer



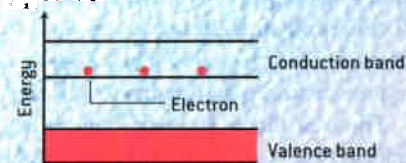
Electron

Sodium ion

Insulator



Conductor



tor array built entirely by ink-jet printing [see illustration on preceding page]. The transistors are larger than their silicon cousins and switch more slowly, but their mobility—0.1 square centimeter per volt per second (cm^2/Vs)—is only a factor of 10 lower than that of amorphous silicon, which is widely used in the backplanes of liquid-crystal computer displays. (Mobility is a measure of how readily charge carriers such as electrons travel in a material. A factor of 10 is a relatively small difference; amorphous silicon lags behind crystalline silicon by a factor of 1,000.)

Dow, Motorola and Xerox have formed an alliance to develop polymer inks and printing methods, as have DuPont and Lucent Technologies, as well as Universal Display Corporation and Sarnoff.

At the 2003 Society for Information Display Conference, Plastic Logic demonstrated what it claimed to be the first plastic-electronics ink-jet-printed active-matrix display. (In active-matrix displays, each pixel is powered by its own transistor.) The display, which had a 63-by-48 array of pixels on a glass backplane about two and a half centimeters square, used the electronic paper of Xerox spin-off Gyricon. Plastic Logic and Gyricon are working to increase the display size, improve resolution and move to a flexible plastic substrate.

Thus far the ink-jet-printing process cannot produce transistors as small and as tightly packed together as in the best inorganic chips. But in mid-2003 researchers at Cornell University, using electron-beam lithography on pentacene, demonstrated that properly functioning organic thin-film transistors could be constructed with a channel length as small as 30 nanometers, comparable to the channel lengths in today's silicon transistors. (The channel is where an electric current flows through a tran-

sistor—or not—and where the switching action takes place.) Previous attempts at making ultrasmall organic thin-film transistors had been successful only down to 100 nanometers; smaller devices had exhibited impaired performance. Electron-beam lithography is an expensive process and would not be the method of choice to produce organic devices commercially, but the Cornell work demonstrates that such small devices are possible.

Organics have other shortcomings in addition to size. One drawback is the lack of a suitable material for making *p*-type and *n*-type transistors together on a single chip, a prerequisite for what is called complementary metal oxide-semiconductor (CMOS) technology, which is the mainstay of microprocessors. (In *p*-type semiconductors the current carriers are holes; in *n*-type, electrons.)

In addition, many polymer materials are fragile, susceptible to damage by humidity or mere exposure to oxygen in the air. This weakness can be addressed by sealing the active components inside airtight and moisture-tight layers, but that solution adds further steps to fabrication and impairs desired properties such as thinness and flexibility.

Some progress has been made in developing sturdier materials. In April, Beng Ong of the Xerox Research Center of Canada announced the development of a polythiophene ink that is not sensitive to oxygen; it can be used to print circuitry without needing a special inert atmosphere.

A sturdy organic-inorganic hybrid was developed by David Bocian of the University of California at Riverside. In November 2003 his team reported that organic molecules called porphyrins, which are made of strings and rings of carbon atoms, could be bonded to the oxidized surface of a silicon substrate. The por-

Organic semiconductors' slower switching speeds are more than adequate for driving displays.



phyrins could withstand up to 400 degrees Celsius for 30 minutes.

One way to avoid damaging the fragile organic part of a device during fabrication is to separate the production of the organic part from the patterning of the other circuitry involved. This method was reported in March by John Rogers of the University of Illinois and his co-workers from Lucent and Rutgers University. They used vapor deposition to lay down thin gold electrodes onto a flexible rubber substrate. This stamp was pressed against a large, high-quality crystal of rubrene to form a transistor. (Rubrene is four benzene rings in a chain with four more attached individually as side groups like two pairs of wings.) The technique avoids exposing the organic crystal to the harsh conditions of the electrode deposition and thereby prevents damage.

The group recorded the highest mobility rates ever seen in an organic transistor—up to $15 \text{ cm}^2/\text{Vs}$. The stamp process might have commercial applications, but it was developed for research purposes. The scientists could remove and reposition the stamp repeatedly. By changing its orientation, they determined that the mobility depended on the direction of travel through the crystal, an effect long expected in the organics field but never before so clearly demonstrated.

Displays and RFIDs

IN GENERAL, organic semiconductors have lower mobility than their inorganic counterparts do, resulting in slower switching speeds. Clock frequencies up to hundreds of kilohertz might be achievable, but don't look for gigahertz-rated organic chips anytime soon. Those speeds, however, are more than adequate for driving displays.

Products containing the first rudimentary displays using conductive plastics are now selling, including a Kodak digital camera with a five-centimeter plastic-electronics view screen and a Philips electric shaver that shows battery charge. Both organic (small-molecule) and polymer (large-molecule) light-emitting diodes can serve as the pixels of a display in a way that is impractical with LEDs made of silicon. The transistors that control each pixel can also be made of plastic semiconductors [see "Better Displays with Organic Films," by Webster E. Howard; *SCIENTIFIC AMERICAN*, February].

ELECTRONIC PAPER produced by Philips has a resolution of 85 pixels per inch and can be rolled up into a cylinder four centimeters in diameter. The paper uses pentacene thin-film transistors that are manufactured at room temperature from a liquid solution. The transistors operate fast enough to display video.

Another display application is electronic paper, in which the display is reflective instead of emissive, made up of tiny beads or microcapsules that change between white and black states [see "The Electronic Paper Chase," by Steve Ditlea; *SCIENTIFIC AMERICAN*, November 2001]. Rigid versions of electronic paper are already in use as programmable displays in department stores. In January, Polymer Vision, a division of Royal Philips Electronics in the Netherlands, released a prototype that combines the e-paper developed by Massachusetts-based E Ink with a flexible, paper-thin backplane of 80,000 organic transistors. The device is a rectangular screen measuring 12.5 centimeters diagonally. Merely three times the thickness of paper, it can be rolled into a four-centimeter-diameter tube [see illustration below]. The circuitry of the device is entirely plastic, except for some ultrathin gold wiring. This is the first flexible display to be mass-produced; 100 are rolling off Polymer Vision's pilot production line every week.

Plastic electronics will also soon be coming to market in radio-frequency identification tags (RFIDs). Metal and silicon-based RFIDs are already in use in automatic toll-payment systems. When a car passes through an RFID-equipped toll plaza, a reader sends out a radio signal that activates the RFID chip in a card on the car's windshield. The card responds with a code that identifies the car, and the toll is deducted from the corre-





PRESSURE-SENSITIVE "SKIN" could give robots a sense of touch. Developed by Takao Someya and his co-workers at the University of Tokyo, each sensor is about three millimeters square. Individual square patches of sensors can be linked up to cover larger areas simply by taping them together with their electrodes aligned. The transistors controlling the sensors are made of pentacene.

Meeting (IEDM), researchers from Infineon described two different types of memory chip based on organic polymers. One was a form of nonvolatile memory, meaning one that retains its data when the power is turned off. Infineon investigators demonstrated that their chips could retain data for more than a year and claimed that the material could potentially be patterned with features as small as 20 nanometers.

The second was a type of dynamic random-access memory, or DRAM, in which each data bit consists of a transistor and a capacitor. Feature sizes were about 140 nanometers. The DRAM was made by a modified form of spin-coating, using a new polymer that is stable even above 450 degrees C, much higher than most conductive polymers can withstand.

Conducting plastics could also be at home in a very different type of device: the chemical sensor. Traditional versions of these have perhaps a dozen electrodes coated with polymer composites, such as polymers mixed with carbon black. Each electrode has a different type of polymer, and when these compounds are exposed to a specific gas, each one responds idiosyncratically—absorbing more or less of the gas in question. This occurrence in turn swells the polymer and alters the conductivity caused by the carbon particles. The pattern of conductance variations across the dozen polymers provides a signature for that specific gas.

Similar effects can be achieved using conducting or semi-conducting polymers instead of the carbon-black composites. These conductive polymer sensors can operate straightforwardly by the change in electrical resistance of the polymer, but they can also be fashioned into capacitors or field-effect transistors whose characteristics change according to which gas has been absorbed into the polymer. Sensors made with conductive plastics could have greater sensitivity than the old composite

sponding account. At present, the cost of such silicon-based RFID tags is around \$0.25, which is low enough for something like a toll-payment system but far too expensive for other proposed uses, such as the tagging of every item in a supermarket to facilitate stock tracking and customer checkout. Plastic RFID chips could bring the cost down to a penny or less, making their ubiquitous use in place of bar codes more viable. [See "RFID: A Key to Automating Everything," by Roy Want; SCIENTIFIC AMERICAN, January; and "Penny-wise Smart Labels," by Steven Ashley; Innovations, on page 30.]

Memory, Noses and Skin

BEYOND LEDs for displays and RFID chips, organic circuitry has many other potential applications. For example, in December 2003 at the annual International Electron Devices

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versions; the transistors in particular could function as built-in amplifiers of the polymer response. A component's response to gases could depend on the detailed structure of the transistor as well as the type of polymer used. In 2001 Ananth Dodabalapur, now at the University of Texas at Austin, and his co-workers demonstrated such sensors using thin-film organic transistors. None are yet on the market. More recently, Dodabalapur has been studying nanoscopic chemical sensors. He has found that transistor-based sensors with channels as small as about 10 nanometers respond in a distinctly better fashion than larger sensors do.

Such sensors could be incorporated into the fabric of a person's clothing for wearable electronics. As reported at the 2003 IEDM conference, Vivek Subramanian and his colleagues from the University of California at Berkeley have demonstrated how to build transistors directly onto fibers. (His group has also worked on chemical sensors.) The transistors were actually made of a mixture of materials, including aluminum threads and gold contacts. The channels of the transistors were made of flexible pentacene with a mobility of $0.05 \text{ cm}^2/\text{Vs}$. Transistors were formed at every intersection of the crossed fibers. The entire fabrication was additive: laying down fibers and depositing other layers on them. By avoiding the need to etch away patterns, as occurs in conventional lithography, the process remains practical for scaling up to large areas of material.

Even though the transistor gates used an inflexible oxide as an insulating layer, the textile could be curved to the equivalent of a 15-centimeter cylinder without greatly impairing the transistor characteristics. Replacing the oxide with a flexible organic insulator should allow even tighter curvature.

One can imagine fabrics made of electronic textiles with controllable properties, including color for camouflage or information display, porosity to control sweating, and other changes to effect heating or cooling. Such wearable computers could also monitor the individual's vital signs or the surrounding environment. The network of threads would allow ripped or damaged fabrics to route signals around the broken region.

Much work remains to realize those goals. To begin with, the transistors need to be more durable to withstand bending and flexing of the material. Such applications do not, however, require high performance of the transistors.

If computerized clothing doesn't interest you, how about electronic skin? In November 2003 Takao Someya and his co-workers at the University of Tokyo announced the use of pentacene transistors in a flexible sheet to form a pressure-sensitive

skin that could be used to give a robot a sense of touch [see illustrations on opposite page]. The pressure-sensitive part of the structure is a layer of carbon-rubber composite with a resistance that varies depending on how much it is compressed. That resistance change switches on an underlying transistor. The team produced units, each consisting of an array of 16-by-16 sensors, each sensor about three millimeters square, along with transistors for extracting the signals from the rows and columns.

To cover a larger area, units can be connected just by overlapping the electrodes at their edges and applying adhesive tape, but there is no reason why larger sensor units could not be made. The entire structure is made completely out of polymers and pentacene with the exception of gold electrodes and a copper coating that lies next to the carbon-rubber composite layer. The units can be bent down to a five-millimeter radius, good enough for encircling slender fingers. A shortcoming of the present design is the poor stability of the sensors' transistors—after only a couple of days their response degraded. Ideally, the sensors should last for months or years. Another problem is a high operating voltage—40 volts—which the researchers hope to lower to 10 volts.

Robots are not yet commonplace outside of industry, hobbies and toys (such as Sony's robot dog, Aibo). The U.N. Economic Commission for Europe estimates that only 50,000 domestic robots (mostly lawnmowers and vacuum cleaners) had been sold worldwide by the end of 2002, but they predict the number will grow by more than a factor of 10 by the end of 2006. Along with robots, smart appliances and products bristling with displays and sensors will increasingly pervade everyday life. Organic electronics will play a crucial role as this responsive, interactive future comes to fruition. ■

Graham P. Collins is a staff writer and editor.

MORE TO EXPLORE

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