



CIRCUITS ON CELLULOSE

PAPER ELECTRONICS COULD PAVE THE WAY TO A
NEW GENERATION OF CHEAP, FLEXIBLE GADGETS

BY ANDREW J. STECKL

YOU WAKE UP with a heavy head. Was it the half dozen glasses of champagne last night or are you getting sick? In your bathroom is a little strip of paper that can tell you for sure. You place it on your tongue and after a few seconds, you pull it back to see the bad news: There's a small green dot next to the word "flu." When you fish your doctor's business card out of your wallet, you notice it looks different from the last time you looked at it. The phone number for his office was originally black. Now it's displayed in blinking red letters, a sign that the number was changed recently.

The electronics in this scenario are not far off; in fact the basic technological breakthroughs needed to make them work have all been achieved in the past few years. At the moment the costs are still too high for them to be used in things like business cards or package labels, but remarkable advances in materials science and simpler fabrication methods are setting the stage for a whole new breed of cheap, bendable, disposable, and perhaps even recyclable electronics. And some of the most exciting work in this field is happening with paper.

At first glance, paper might seem like an unlikely front-runner in the flexible electronics race. Straight off the shelf, the material isn't nearly as rugged as plastic or as smooth

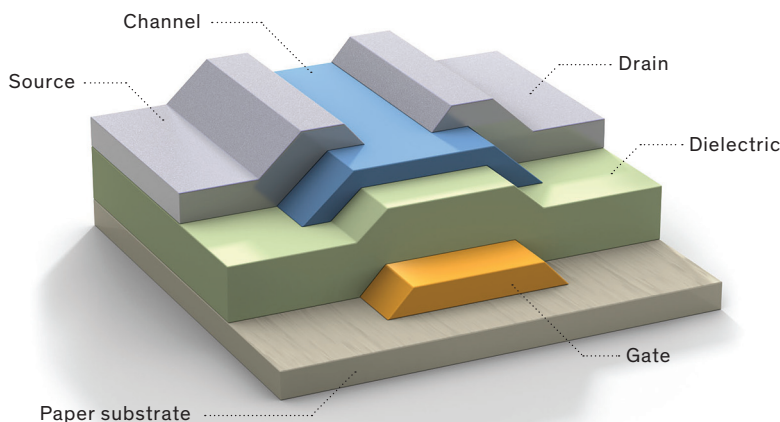
Transistors

as new, bendable forms of glass. And at a microscopic level it's just a tangle of cellulose fibers, hardly the sort of structure that's ideal for making a bunch of finely featured, identical circuit components.

But paper actually has a lot going for it. It's lightweight, flexible, biodegradable, and it comes from a renewable resource. It's also extraordinarily adaptable: With the right set of additives and manufacturing processes, paper can take on a seemingly endless range of properties. It can be made hydrophilic or hydrophobic, porous or watertight, opaque or nearly transparent, delicate or strong, coarse or about as smooth as glass.

Paper electronics also have the potential to be extraordinarily cheap. The material itself is intrinsically inexpensive; conventional varieties cost about a tenth as much as plastic film. Even the special paper that's tailor-made for electronics costs, area for area, about 1 percent as much as silicon. Roll-to-roll presses can print microscopic features on wide reams at speeds of up to 30 meters per second—about three times as fast as the Olympian Usain Bolt can run.

When my research group at the University of Cincinnati first started working with paper in 2008, we weren't thinking too broadly about the material's potential as the base layer, or substrate, for electronics. We were originally interested in a relatively narrow application, what might be called "e-paper on paper," essentially electronic displays built directly on paper. The initial proof-of-principle experiment worked far better than we expected, and in the years since, I've become convinced that paper's potential could be just as broad (if not as deep) as silicon's has turned out to be. Paper has already shown promise as a substrate for sensors, biological assays, RF antennas, batteries, circuit boards, and smart packaging labels. In the next few years, we'll start to see the first gadgets based on this technology make their way out of the laboratory and into the hands of consumers and business users.



FLEXIBLE STACK: Transistors on flexible substrates can be built using organic or inorganic semiconducting channels. This schematic illustrates a way of making an organic switch.

IN A TECH WORLD dominated by plastic, glass, and silicon, it may come as a surprise to learn that research into paper electronics actually dates back nearly 50 years. In the late 1960s, Peter Brody's group at Westinghouse Electric Corp. experimented with paper, among other materials, as a substrate for thin-film transistors, the sort that could be built into switching arrays to control individual pixels in a liquid-crystal display.

Even then, before a wealth of coating and processing innovations came on the scene, paper had a number of attractive attributes. Chief among those was its quality as an electrical insulator. Paper generally boasts a resistivity of some 10 billion ohm-centimeters, about 100 000 times the intrinsic resistivity of silicon. That means the material should, in theory, work quite well as a substrate for electronic devices. It resists the flow of current so well that it effectively eliminates one of the most common pathways electrons use to sneak across a transistor when it's supposed to be off.

That isn't to say paper is the ideal material on which to build transistors. Materials like glass and traditional semiconductors are easy to manufacture with variations in surface height of a few nanometers or less. But height variations in paper range from at best a fraction of a micrometer up to several micrometers, depending on the fiber size and how well those fibers commingle to form a flat mat. Electronic devices built on such an irregular surface are likely to vary greatly in performance, and a sizable proportion will not work at all.

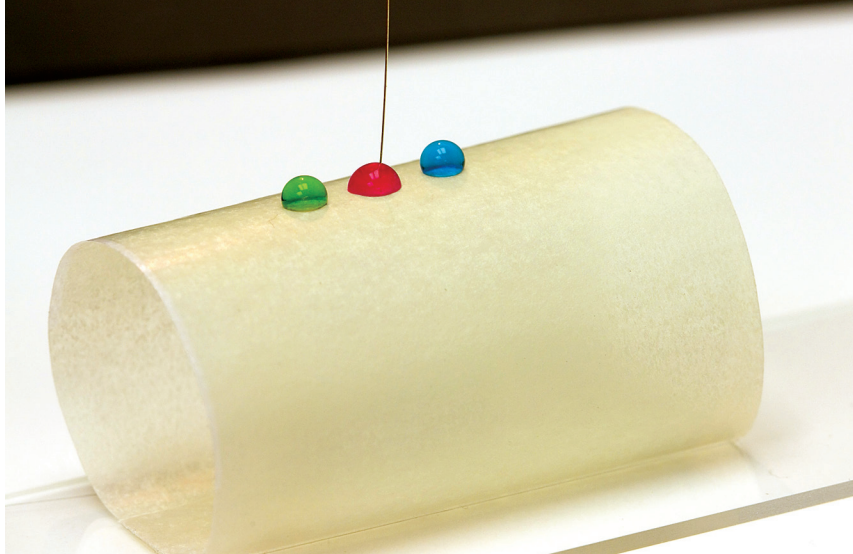
Despite that, about five years ago, as interest in electronic readers and flexible reflective displays took off, researchers began to explore paper as an electronics substrate. The potential payoff was big: If they could build the back-end circuitry needed to control pixels, they'd be halfway to creating a changeable reflective display that naturally has the look and feel of paper (and is just as thin, lightweight, and flexible).

Since then, about a half-dozen research groups have made considerable headway in constructing paper-based transistors. They've used either inorganic semiconductors like silicon or indium gallium zinc oxide for the current-carrying channels or organic materials like pentacene or P3HT. A good part of this progress has followed from finding

or developing the right kinds of paper. The best are those that have special polymer coatings that help fill in troughs in the surface and seal the paper to prevent chemical degradation during the fabrication process.

Paper would simply combust at the temperatures used to grow and treat the crystalline films used in traditional semiconductors, so inorganic paper-based transistors are typically made from amorphous, noncrystalline films. These can be formed at a lower temperature using the standard techniques of depositing a material in a vacuum, such as evaporation or sputtering. This fabrication strategy is straightforward, but the resulting transistors tend to embrace paper's inherent textural variation, the result being that the voltage needed to get current to flow in them can be a dozen times as much as what's needed to move electrons through transistors built on glass or silicon. John Rogers's group at the University of Illinois at Urbana-Champaign, for example, has been perfecting an alternative approach in which circuits are built on silicon and then transferred to paper (or other substrates) once they're finished. This method tends to create better-performing circuits, although the fabrication process is considerably more involved, and it's also more costly, because it would start with a silicon wafer.

When it comes to mass production, however, the organic semiconductors may be the way to go. Unlike inorganic materials, organic compounds can be dissolved in fluid and deposited on paper using roll-to-roll printers, just as with ordinary ink. But this approach still faces some obstacles. For one, the transistors tend to be slower, due to the intrinsic properties of organic semiconductors. And organic switches are naturally more sensitive to environmental conditions. Oxygen and water vapor, for example, can degrade or even open up a gap between an organic material and a metal electrode through chemical degradation by oxidation or by partially dissolving the structure. Surface treatments can help make paper—which naturally sops up moisture from the air that could affect the device built on top—relatively impermeable. But a fix is still needed to ensure that organic circuits perform well over long periods in relatively humid environments.



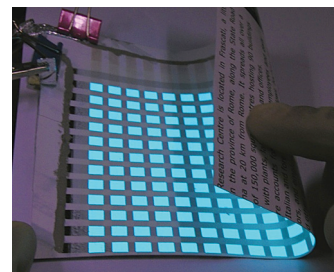
Pixels

THIN-FILM CIRCUITS BUILT on paper are too slow to be considered for general purpose computing, but they are an attractive means for controlling and interacting with “outward-facing” devices such as sensors, displays, and energy-harvesting gear.

Building such devices on paper can be just as challenging as building back-end electronics. But there has been a lot of progress, particularly in the relatively inexpensive and low-power realm of reflective displays. One promising approach is the electrochromic display, which uses pixels made of a conducting polymer. If a sufficient voltage is applied to such a pixel, electrons will be knocked off and the optical properties of the polymer will change, turning it from, say, dark blue to transparent. This approach, which was pioneered by Magnus Berggren's group at Linköping University, in Sweden, has many advantages. For one, it requires just a few volts to operate, and it's structurally fairly simple. But there are a few drawbacks. The color palette is limited, and the switching speed is quite slow. It can take anywhere from a fraction of a second to several seconds to complete pixel transformation, which makes the display unsuitable for full-motion video.

At the University of Cincinnati, my group has been working on adapting an alternative display approach called electrowetting, which is traditionally used with glass. Electrowetting works by confining liquids between two surfaces and then altering their surface tension, using an applied voltage. Altering the surface tension causes the colored liquid to either spread out and reflect light or ball up and allow the light through. Paper hardly seems a natural fit for this technique. Electrowetting displays typically use liquids like water and oil that are readily absorbed by paper. Pixels also need to be built on a very smooth, glass-like surface to ensure reliability and fast response. With a rough surface, it's very hard to guarantee that liquids will move where they're supposed to every time.

We first tried the same sort of wax-coated papers that you might find in your kitchen cupboard, standard “smooth-finish” commercial papers, and also a translucent paper called glassine. Although the surfaces of all these paper



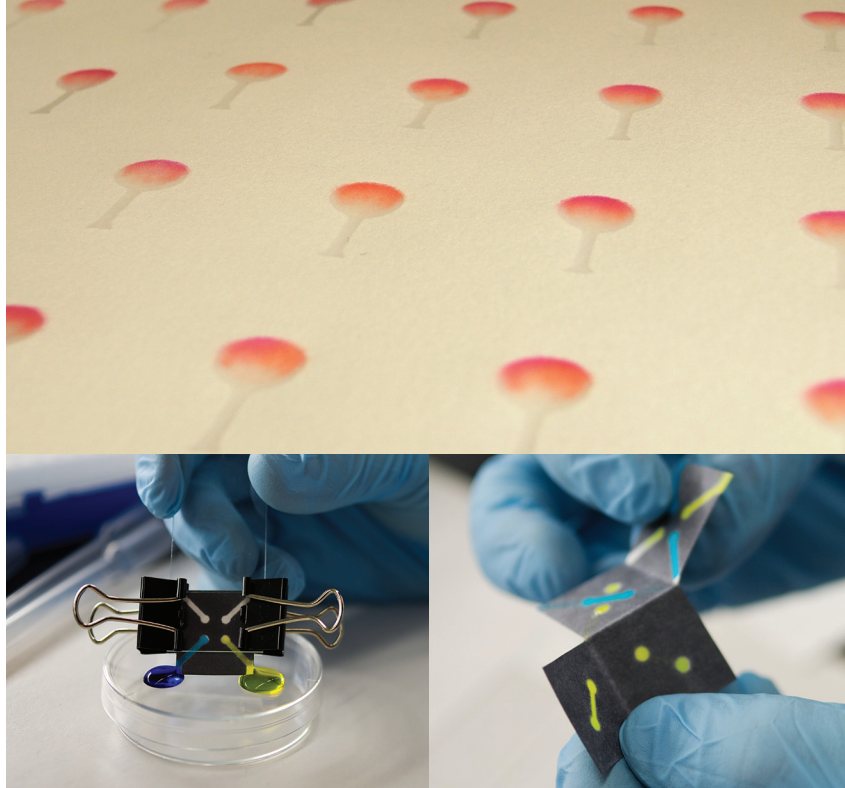
ON DISPLAY: Paper can be used to make displays that either reflect incoming light or emit their own.

One way to make a reflective display is to alter the surface tension of liquid pixels [top]. Organic light-emitting diodes can also be built on paper to make displays that glow [bottom].

types resist water, they eventually did absorb the liquid. Then we were contacted by the Boston-based Sappi Fine Paper North America, which had created a polymer-coated paper with an average surface roughness of a couple of nanometers, just a little higher than that of glass. That seemed to be just the thing. With that material, we were able to make reliable pixels with switching times as short as 10 milliseconds—nearly suitable for video. We are now working to develop paper-based displays using electro-wetting. We think this approach might be ideal for smart labels on packages that could, for example, show videos about how the product is to be used, or for displays—containing vital information for soldiers in the field—that can be rapidly destroyed if necessary.

For both displays and back-end electronics, fabrication still remains a problem. The fastest, cheapest way to build paper electronics is to use a roll-to-roll printer. But the state-of-the-art resolution of these machines is currently about 10 micrometers. So flexible electronics fabricated with these machines would have feature sizes about the same as those of silicon-based chips in 1971, when microprocessors had about 2000 transistors. Improving this resolution without sacrificing printing speed will take years and significant investment.

That being said, size isn't everything. Displays—particularly if they can be constructed economically—can still be quite readable and attractive even if they're constructed from components that are much larger than those needed for advanced integrated circuits. (After all, today's state-of-the-art tablets and e-readers boast pixel sizes of about 100 μm , which is about 10 000 times as large as the minimum feature sizes needed to build state-of-the-art memory chips.) Some circuit components need larger features to function well. Radio-frequency ID tags, for example, need relatively large antennas to be able to pick up and transmit electromagnetic waves with radio wavelengths. Even the smallest RFID chips reported to date are about 50 μm on a side. And high-voltage power electronics tend to perform better when they're made bigger, because spreading a load over a large area reduces the chance of electrical breakdown. This is a realm where paper has already been used for many years, as an insulator in transformers.



Microfluidics



THOSE OF US building paper-based electronic devices and displays are, to a certain extent, working against paper's intrinsic properties. But there is one potential application area where paper is clearly a natural fit: microfluidics.

Microfluidic devices work by transporting liquids from one spot to another. In the realm of biomedical technology, they're particularly useful because they allow you to perform tests like DNA analysis or toxin detection on small liquid volumes, which cuts down on costly chemicals and reagents and greatly reduces the

amount of bodily fluids that must be extracted from patients. To date, most microfluidic units have been high-precision affairs that rely on plastic feed tubes and externally powered pumps, which can take up a fair amount of counter space. If patterned correctly, paper could be used to perform similar tests without these external accessories. The narrow channels between fibers in paper excel at drawing in water and other fluids automatically by capillary action.

Some companies have already taken advantage of this liquid-wicking capability to create disposable pregnancy and blood-sugar tests. But recently the emphasis has shifted to a "bottom up" approach. Instead of making inexpensive versions of specific tests, researchers are now trying to develop a general class of paper-based microfluidic systems that can then be adapted to make a variety of different tests, for such tasks as monitoring liver function or diagnosing tuberculosis. If done right, these tests could be compact, self-contained—and cheap. They could also be used without a great deal of training, at home or out in the field. **| CONTINUED ON PAGE 60**

CHANNELING LIQUIDS: These basic microfluidic sensors [top] are built on filter paper. Straight channels lead to circular sensor regions that turn red in the presence of nitrogen dioxide. A single sample can be tested in multiple ways as it moves through a 3-D microfluidic device, like this one [bottom], which was built through folding.

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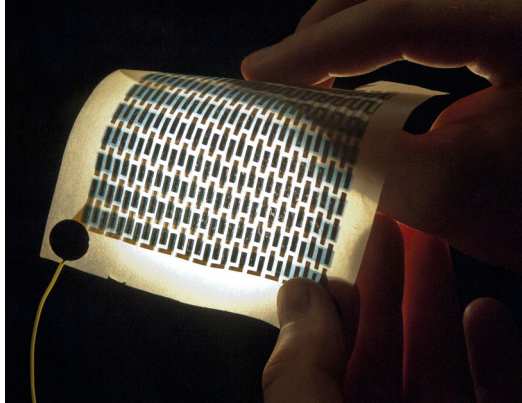
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CONTINUED FROM PAGE 52 | and easily disposed of by incineration after one use.

Two of the pioneers in this field are George Whitesides at Harvard University and Paul Yager at the University of Washington. Both have benefitted from early and sustained support by the Bill & Melinda Gates Foundation for developing simple and very-low-cost diagnostic devices that do not require special skills or facilities. Their groups have advanced several simple and elegant approaches to forming paper microfluidic devices. One approach relies on a wax-based patterning process, which uses an inkjet printer to place features on paper with a wax-based "ink." After printing, the paper is heated to drive the wax through the entire thickness of the material. Because the wax-impregnated regions are hydrophobic, fluid flow is restricted to wax-free regions. Wicking eventually guides the liquid to be tested into dry "compartments" containing chemical reagents or biomarkers. If the right combination of compounds is present, a chemical reaction takes place, producing a color change that the user can then read. Three-dimensional versions of these units have been developed in order to create compact packages that can perform multiple tests, in different layers, on the same sample or else redundant tests to reduce the chance of a false result. One recent innovation comes from Richard Crooks's group at the University of Texas at Austin, which found a way to construct many-layered paper fluidic devices out of a single sheet of paper. The team's origami-like approach starts with a two-dimensional hydrophobic pattern that is formed using photoresist. After a few selective snips with scissors and some folding (think paper doll construction), a multilayered square can be assembled without tools. In the resulting assembly, overlaid openings allow fluid to flow up through as many as nine layers.

These paper-based tests have already spawned spin-off companies and nonprofits and will probably be the first paper-based technology to be commercialized. I expect they could eventually be augmented with communications circuitry and some logic to make remote sensors. But there is still much to learn about the actual fabrication costs of these assays, as well as practical properties like shelf life, sensitivity, and the reproducibility of their results.



PAPER POWER: Flexible, foldable arrays of solar cells can be built on a paper substrate using vapor deposition. The solar array pictured here incorporates five layers and uses organic photovoltaic materials to convert light into electricity with roughly 1 percent efficiency.

Integration



THE DISPLAYS AND microfluidic systems I've described are far from the only applications being explored. My group and others, for example, are actively building light-emitting devices on paper to make luminous displays [see images, "On Display"]. Others are investigating novel ways to construct flexible RF antennas attached to curvilinear surfaces that boost their performance. Of course, regardless of what we choose to build, paper electronics will always be limited unless we can find a way to deliver power to the devices in a way that's just as mobile, thin, lightweight, and flexible as paper itself. What we'd really like to do is build batteries, capacitors, or photovoltaic cells directly onto the same paper that bears the devices.

One potential way to store energy on paper is to take advantage of its long, thin cellulose fibers, which offer a lot of surface area that could potentially be used to store charge. Paper can be soaked with electrolytes to make a variation on the traditional battery. Alternatively, it can be coated with inorganic metal or carbon to store charge. The work is far enough along that it is being pursued commercially by firms such as the Paper Battery Co., in Troy, N.Y., Power Paper, in Israel, and EnfuCell, in Finland. The storage specifications already seem promising: a 1-millimeter thick, 10- by 10-centimeter square patch can store a few hundred milliamperes hours at 1.5 volts, about 10 to 20 percent the capacity of a typical AA battery.

Once all these components—power, back-end electronics, and front-end devices—are in place, I believe it will be possible to develop fully integrated, complete systems on paper that can power themselves and communicate with the outside world.

But finding ways to perform this integration will be a significant challenge. The ideal paper substrate for back-end circuitry might be very

different from what's required to build, say, a front-end display or marry a microfluidic device with logic and communications circuits. Certain features, in particular the wires used to connect components, are especially fragile and will have to be carefully constructed, probably using materials and geometry different from those in conventional rigid integrated circuits.

But think of the possibilities if we succeed. We could fill an important economic gap in the technological spectrum of electrical devices, between the low-tech realm of incandescent lightbulbs and electric motors and the high-tech world of computer chips and flat panel displays. Although the cost of making an individual transistor has been declining for decades, the overall fixed costs of materials, fabs, and equipment are substantial and growing. We need a fundamentally new approach if we want to shake up the industry.

Paper is likely to emerge slowly in electronics: You'll see it first in markets where low cost—not high performance or small area—is the main consideration. Along the way, paper will face competition: Plastic is more rugged and electronics-friendly, and glass can now be made so thin and bendable that it's not impossible to imagine it could one day be fed into roll-to-roll machines. Despite this, paper has the potential to extend the reach of electronics into areas we might never have considered before, offering consumers a much wider range of choices when it comes to performance, reliability, and price. On paper (if you'll pardon the pun), there's little reason to think that this technology will stay in the lab for long. ■

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