

Brenner have examined quantitatively, although they do make a qualitative extension to the case of two spheres between two parallel confining walls. For two spheres that are precisely in the midplane between the walls, the hydrodynamic effects from each wall will cancel by symmetry. But Squires and Brenner argue that if the spheres are slightly off center, which is almost inevitable experimentally, the hydrodynamic effects won't exactly cancel and could produce an apparent attraction of the magnitude observed in earlier measurements by Grier with John Crocker.

Because the hydrodynamic theory

is applicable only to nonequilibrium measurements, there is no direct implication for the bulk equilibrium measurements that have also shown evidence for attractions between colloidal particles. To the extent that Squires and Brenner's model does indeed account for the observed two-sphere behavior near a single wall, it indirectly sets limits on the influence of electrostatic or other effects that could also be playing a role, both in that system and in the bulk. Meanwhile, a consensus is emerging that many-body effects originating in counterion correlations are at the heart of the observed attraction in the bulk.

The jury is still out on the value of wall charge density, which will determine the extent to which hydrodynamic effects account for the observed behavior of two charged spheres near a wall. Grier is working closely with Squires and Brenner to reevaluate his old experiments and perform new ones aimed at settling this issue, for both one-wall and two-wall systems.

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New Printing Technologies Raise Hopes for Cheap Plastic Electronics

Semiconducting polymers might not compete with silicon for speed and durability in electronic circuits but they are candidates for applications in which low cost and flexibility are paramount—such as large-format displays or bar codes that can be remotely interrogated. In quest of cheap polymer electronics, researchers over the last five years have progressed from making fairly rudimentary single all-polymer transistors,¹ to turning out high-performance integrated circuits made all,² or nearly all,³ from plastics (see PHYSICS TODAY, November 2000, page 9). The large-scale circuits were patterned by relatively expensive techniques such as photolithography.

Two groups have now demonstrated alternative, cheaper printing methods—stamping and inkjet printing—done outside a clean room. John Rogers and his coworkers from Bell Labs, Lucent Technologies, have used a rubber-like stamp to pattern an active matrix of 256 polymer transistors on the backplane of a flexible optical display,⁴ as they reported at the Materials Research Society meeting in Boston in late November. In addition, Richard Friend and his colleagues from the University of Cambridge have used high-resolution inkjet printing to produce thin-film transistor circuits, with fewer transistors but with electrical interconnections between layers.⁵ Other teams are working on similar printing methods. The new methods are not ready for commercial debut, but the progress is encouraging.

George Whitesides of Harvard University, whose lab has developed microcontact printing (stamping),⁶ asserts

▶ Inkjets and rubber stamps just might replace expensive photolithography steps in the printing of polymer circuits. If so, we may one day read our newspapers off reloadable, flexible plastic sheets.

that plastic printing methods are potentially “real technology dislocators.” He adds, “polymers are increasingly looking as if they can do things that inorganics just can't do.”

The lure of solution chemistry

Researchers have aspired to make electronic circuits with organic materials ever since they learned to turn polymers into conductors and semiconductors (see PHYSICS TODAY, December 2000, page 19). The lure is the ease of processing polymeric thin films with solution chemistry. Another attraction is the flexibility of plastic substrates, which should allow large-area circuits to be printed in a continuous manner on sheets that are rolled onto and off of large reels.

A key building block of electronic circuits is the transistor. The semiconducting layer in a field-effect transistor (see figure 1) might be made of one polymer and the source, drain, and gate electrodes of another, conducting, polymer. A thin film of the semiconducting polymer can be easily applied to the device. The electrodes, however, require patterning and, for inorganics such as metals, that step has traditionally been done with lithographic and etching techniques. For low-cost plastics, however, photolithography is not a good choice because it is relatively expensive, incompati-

ble with some polymers, difficult to apply on uneven substrates such as flexible plastics, and not appropriate for reel-to-reel processing. These drawbacks have motivated the search for alternative printing methods.

At Philips Research Laboratories in Eindhoven, the Netherlands, a team led by Dago de Leeuw has developed a version of photolithography called photochemical patterning. In the place of a resist, the experimenters expose a light-sensitive polymer to ultraviolet light through a mask. The regions exposed to the UV light change from conducting to nonconducting, defining the desired pattern. According to Philips researcher Bart-Hendrik Huisman, their technique is cheap due to the high throughput, does not require a vacuum, and can be used on flexible substrates, as they have shown with their all-plastic integrated circuit.²

Nevertheless, other researchers want to pursue possibly cheaper methods that are capable of printing on a larger variety of polymers. These alternatives must be able to pattern sufficiently small feature sizes. The critical dimension is the distance that the field-induced charges must traverse—the distance between the source and drain. For the polymers typically used, that distance must be on the order of 10 μm to give acceptably high drive current and switching speeds.

Microcontact printing with elastomeric, or rubber-like, stamps, does have the required resolution. The Bell Labs group has used it to pattern organic transistors;⁷ the new work extends their capability to a much larger scale (15 cm $\times$ 15 cm). To date,

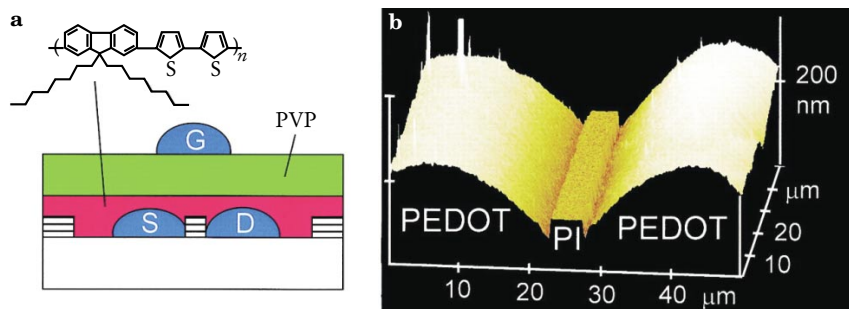


FIGURE 1. FIELD-EFFECT TRANSISTOR formed by inkjet printing. (a) Schematic of the transistor structure. The source (S) and drain (D) electrodes (blue) are formed from droplets of a conducting polymer sprayed by an inkjet printer and confined by repelling “walls” of polyimide (striped regions). A semiconducting polymer (magenta) is laid down over the two electrodes, and a layer of PVP, a dielectric insulator (green), on that. A voltage on the gate (G) induces charges in the semiconductor and allows current to flow from source to drain. (b) Atomic force microscope trace of the source and drain region shows the electrodes, made of a polymer called PEDOT, separated by a 5- μm wide wall of polyimide (PI). (Adapted from ref. 5.)

inkjets have not had 10- μm resolution, but the Cambridge group devised a way to get it.

Microcontact printing

Rogers and his Bell-Labs colleagues patterned an active-matrix display, in which each pixel is controlled by an individual transistor. Their array of field-effect transistors forms the backplane of a flexible plastic display (see figure 2). For the display elements at the front, the researchers used pixels made from microencapsulated electrophoretic “inks” developed by E Ink Corp of Cambridge, Massachusetts. The titanium-oxide nanoparticles inside each capsule respond to the electric fields from the associated transistor, making the capsule appear white or black as they move toward the front or the back.

The transistors in the Bell Labs array have gate electrodes on the bottom rather than the top (inverted compared to figure 1). The experimenters used a fairly low resolution stamp to define the gate pattern in a layer of indium tin oxide that covered the Mylar™ substrate. They coated the resulting gate electrodes with a layer of glass to serve as the dielectric.

Next came the critical step: printing of the source and drain electrodes, which requires a higher resolution pattern to keep the source-drain separation as small as 15 μm . The Bell Labs team made its electrodes out of gold rather than polymeric material because gold is known to work well with the “inks” used in stamping (not to be confused with the inks used in the display). The stamp

applied an ink of hexadecanethiol to a thin film of gold that had been evaporated on the glass. The ink molecules formed a self-assembled monolayer on the gold, covering the desired spots with minimal defects and well-defined edges. The unstamped regions of gold were etched away and the remaining ink was evaporated. Finally, a layer of semiconducting polymer was spin cast on top.

Note that photolithography is needed to pattern the elastomeric stamp. Once a stamp is made, however, it can be used again and again to turn out perhaps thousands of circuits. Also, the use of a gold film is not compatible with all-solution processing, but the Bell Labs team has shown it can deposit another metal—

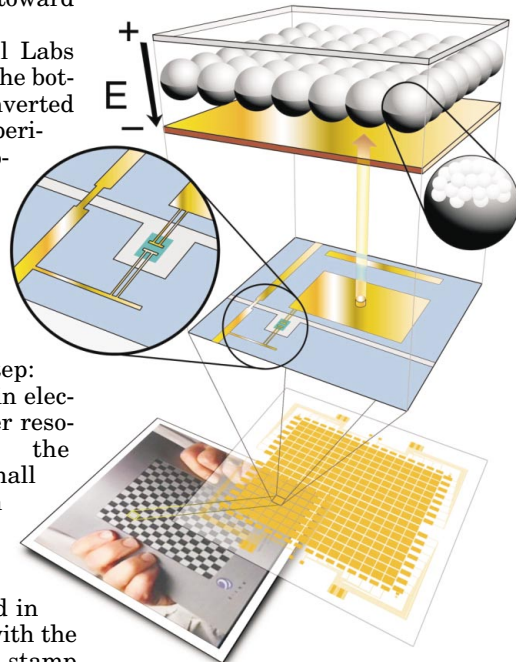


FIGURE 2. FLEXIBLE ACTIVE-MATRIX display, demonstrated here by a checkerboard of square pixels (bottom). Successive enlargement reveals the transistor element (circled) on the backplane. Within the enlarged circle, the green pad is the semiconductor; the gold lines are the source and drain electrodes; and the gray regions are the gate and connecting column electrodes. The transistor turns on the electric field in the display’s top plane, driving white nanoparticles suspended inside each capsule toward the front and turning the pixel white. (Figure courtesy of Bell Labs.)

silver—from solution to make organic transistors.⁸

The Bell Labs group had to master a number of challenges to stamp out an active-matrix circuit having hundreds of transistors with 100% yield. Rogers said it took them a full year of intensive effort to scale up from similar technologies used to produce small circuits.

One challenge was to minimize the registration error, that is, the displacement of a circuit element from its intended position, often caused by strains in the rubber stamps. With little effort, the Bell Labs group kept its registration error to 50 μm , but the error needs to be reduced to 5 μm for display applications with pixel dimensions of 100 μm . Individual feature sizes need to be as small as 1 μm .

Inkjet printing

The Cambridge team made its source and drain electrodes in the bottom layer of its transistor (see figure 1) by depositing droplets of a conducting polymer in solution onto the desired positions. The droplets tend to spread when they hit the substrate, so to maintain a minimal separation of 5 μm between the source and drain, the Cambridge group confined its droplets with tiny walls of polyimide, a hydrophobic polymer. This technique does require an initial photolithography step to define the desired pattern in the polyimide.

Once deposited, the source and drain electrodes were covered with a layer of semiconducting polymer, and then by an insulating dielectric. The gate electrode was put down on top by inkjet printing in air. The transistors made in this way had mobilities that were only one or two orders of magnitude lower than those of conventionally processed amorphous silicon thin-film transistors. They should be suitable for such applications as active-matrix displays or product identification

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tags. So far the Cambridge group has only demonstrated its inkjet printing on a solid, rather than flexible, substrate, and not yet for an integrated circuit.

The Cambridge group also developed a way to make another key component of a complex integrated circuit: via-hole interconnects, which link electrodes, such as the gate and drain, in different layers of the transistor structure. The Cambridge researchers made such interconnects by using the inkjet to deposit successive droplets of isopropanol, which dissolve the insulating layer and excavate a hole that can then be filled with a conducting polymer. Friend thinks that his group's technique to produce a via-hole interconnect may turn out to be one of the most significant aspects of this work.

One advantage of the inkjet printing is that it offers a lot of flexibility in the choice of materials that can be printed in any of the various layers. Another advantage is that it can provide accurate registration over large areas. As currently implemented, however, it still relies on an initial photolithography step.

Friend points out that microcontact and inkjet printing are complementary: Microcontact printing is good at creating a fine-scale pattern, but this pattern is not often directly useful because it does not get the active materials into place. Inkjet printing provides a very versatile means of delivering a wide range of materials to a substrate but does not, by itself, have sufficient spatial resolution. A combination—such as microcontact printing as the first patterning step in the inkjet process—might be desirable.

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