

Making Devices Smaller, Brighter, and More Bendy

BOSTON—Nearly 4000 chemists, physicists, and materials scientists gathered here from 30 November to 4 December to compare notes on everything from nanotubes to nuclear waste at the fall meeting of the Materials Research Society. Among this year's highlights were plastic displays and holey films.

The Kitchen Chemistry of Nanoholes

Computer chip makers spend billions of dollars on fabrication plants to etch fine patterns onto brittle semiconductor chips. But even with the most up-to-date machines, these masters of miniaturization still struggle to create features smaller than 250 billionths of a meter, or nanometers. At the meeting, a team of University of Illinois researchers led by chemist Sam Stupp reported that with the help of some clever chemistry, they can produce semiconductor films punctured with a regular array of holes, each just 2 nanometers across. This pattern isn't as complex or precise as those needed to make computer chips, but it could have many other uses. Says team member Paul Braun, "all this is done with kitchen chemistry."

The new porous films come in two flavors, cadmium sulfide and cadmium telluride. Each looks like a nanoscale version of perfect Swiss cheese, containing an array of holes spaced 7 to 8 nanometers apart in a regular honeycomb pattern. What's more, the tiny holes penetrate through the films, which can be more than 1 micrometer thick, making them 500 times longer than they are wide. Such films could find uses ranging from solar cells to molds for making arrays of nanometerwide wires. "It's beautiful work," says Dan Feldheim, a chemist at North Carolina State University, Raleigh.

Stupp's team—made up of students past and present, including Braun, Mariusz Twardowski, Paul Osenar, and Gregory Tew—began by chemically synthesizing two-part chainlike molecules. One half of each chain contains a water-fleeing (hydrophobic) group, while the other half consists of a water-loving (hydrophilic) group, composed of regularly spaced hydroxyl groups. Hydroxyls tend to

form strong hydrogen bonds to one another, but in this molecule they are separated by single carbon atoms so that they tend not to bind together. Instead, they go looking for hydroxyls on other chains.

The Illinois team gave them that chance by coating a plastic surface with the molecules and then topping them with a thin layer of water spiked with cadmium nitrate. The molecular chains instantly began arranging themselves. The hydrophobic groups sought to escape the water by pack-

ing together in a huddle on the plastic surface with their hydrophilic ends pointing outward. More molecular chains piled on top, forming a cylindrical pile, with all the hydrophobic ends inside the cylinder and the hydrophilic ends dangling in the surrounding water. These cylinders form standing up on end and pack tightly together in a hexagonal lattice to be as close together as possible—an energetically favorable arrangement. Once in this arrangement, the hydroxyl groups on neighboring molecules, which themselves are linked to neighboring cylinders, bond to one another, knitting the cylinders into a continuous film dotted with evenly spaced hydrophobic cylinders.

To convert this pattern into a cadmium sulfide semiconductor, the Illinois researchers relied on the fact that typical metal salts such as cadmium nitrate don't dissolve in oil. In solution, the cadmium nitrate dissociates into cadmium and nitrate ions. And because these ions remained excluded from oil-like, or hydrophobic-rich regions, that left them distributed everywhere in the film except the inside of the cylinders.

To convert the cadmium ions into a semiconductor, the researchers bubbled hydrogen sulfide gas through the porous substrate. As the gas percolated through the substrate and overlying film, it reacted

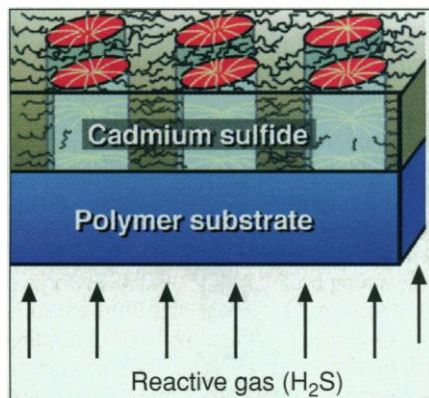
with the metal ions, precipitating out cadmium sulfide, a well-known semiconductor. The team used a slightly different method to create the cadmium telluride (CdTe) film. But here, too, the semiconductor deposited only in hydrophilic regions, leaving the hydrophobic portions clear. In both cases, as the film grew, the holes continued to grow with it, creating an array of tiny pores.

Stupp and his colleagues say the work is so new they're just beginning to test the utility of the porous films. In one quick test, they found that the films work well as molecular sieves, allowing small spherical polymers to penetrate inside their pores while excluding larger ones. The porous CdTe films also proved to be at least four times better than unpatterned CdTe films at converting light to electrical current. That's likely to make them a worthwhile prospect for solar-cell researchers, who are already investigating CdTe film solar cells as a cheaper alternative to the widely used crystalline silicon cells.

The researchers are also getting ready to test a bevy of other ideas, such as filling the holes with metal to produce arrays of nanowires and magnetic materials to create magnetic particles for ultrahigh density data-storage material. These ideas remain to be investigated, but the fact that patterned films can be persuaded to assemble themselves may encourage semiconductor researchers to look again to kitchen chemistry for help.

Closing in On Plastic Displays

The familiar, and expensive, liquid-crystal display in your laptop computer may soon be a thing of the past, as light-emitting elements made from cheap and bendy plastic continue in their relentless progress toward commercialization. At the meeting, Cambridge University physicist Richard Friend, who is also research director of Cambridge Display Technologies (CDT), offered the first close look at his company's latest imaging marvel: a light-emitting plastic video display, 5 centimeters across the diagonal, that is as thin as a single pane of glass. Although the display Friend described glows in a monochrome green, he reported that CDT has



Shot through. Two-part organic molecules template semiconductors into porous films.



Roll 'em. Plastic video displays set for full color.

now developed efficient plastic light emitters in a rainbow of different colors, setting the stage for full-color plastic video displays, computer screens, and televisions.

The new displays are "very impressive," says Yang Yang, a polymer display researcher at the University of California, Los Angeles. "They have combined light-emitting polymers with polysilicon thin-film transistors [TFTs]," he says. TFTs control the electrical current for each picture element, or pixel, in active matrix screens, such as those in today's laptop computers. Because light-emitting polymers are cheap to make and easy to apply over large surfaces, they open the door to making billboard-sized displays, especially if combined with easily printed polymer-based circuitry. This could help polymer devices claim a large portion of the display market, projected to be \$45 billion a year by 2000.

Researchers have previously managed to incorporate light-emitting polymers into less advanced passive matrix displays, which send current to entire rows of pixels at once. But because these displays are slow to change images, they are generally good only for low-information content pictures such as text, rather than complex, fast-moving video images. To take the next step, CDT researchers teamed up with Seiko-Epson, a Japanese firm that makes the silicon-based circuitry for active matrix displays. Today's active matrix computer screens use a trio of filters at each pixel to filter out select colors of light shining through from a white backlight. The filtering is done by liquid-crystal molecules between two panes of glass. A voltage applied across pairs of electrodes, one on each pane, switches the liquid crystals from a transparent to a filtering state. The voltage is controlled by a tiny TFT printed on the glass at each pixel.

The new display does away with one of the glass panes and the liquid-crystal filters. On top of a single glass pane prepatterned with an array of TFTs, researchers spot down an array of transparent electrodes, each wired to its own TFT. This array is then coated with a light-emitting polymer known as poly(phenylene vinylene), or PPV, and an opaque electrode on the top. The array of tiny TFTs controls the current to each pixel. When a TFT turns on, the electrodes inject negatively charged electrons and their positively charged counterparts, called "holes," into the polymers. As the charges migrate toward the oppositely charged electrodes through the intervening polymer, some electrons and holes meet up and combine to give off photons of light, which shine through the transparent electrode and glass.

Creating a display that shines in a single color is quite an achievement, but getting to full-color polymer displays remains a major challenge. One hurdle is that different poly-

mers are needed to emit light in different colors, and they come with a range of properties. For example, although it takes only a small electrical voltage to induce PPV to glow efficiently, the same can't be said for polymers that emit other colors. That's a big problem for displays, says Friend, as it can cause some colors to shine more brightly than others. Last spring, however, chemist Ed Woo of Dow Chemical in Midland, Michigan, reported discovering a new family of polymers that, with a bit of tinkering, can emit colors across the visible spectrum. At the Boston meeting, Friend reported that CDT researchers have used these polymers to make a variety of light-emitting diodes, all of

which, it turns out, emit light with similar high efficiencies and at low voltages.

CDT and Dow have not revealed the exact chemical structure of their new polymers. They will say only that all are derivatives of polyfluorene, and each contains a chain of phenylene rings with a particular side group connected to neighboring pairs of rings. The researchers found that they can tune the color of light emitted from the polymer, from blue through to red, by simply changing the side groups on the polymer chain. Yang calls the new light emitters "a very important step forward for the field," because their near-uniform behavior will make it easier to make full-color displays.

—ROBERT F. SERVICE

PHYSICS

Gravity Measurements Close in on Big G

The precise strength of this pervasive force has proved surprisingly elusive, but conflicting results are finally giving way to a single answer

Two hundred years ago, in a stone house on the outskirts of London, Henry Cavendish weighed the world. By the light of a candle, he watched as a small lead barbell suspended by a fiber twisted minutely under the gravitational tug of two bowling ball-sized weights. The size of the twist revealed the strength of gravity between the two known masses, the barbell and the balls. Because Cavendish knew how strong Earth's tug was, he could then precisely pin down its mass.

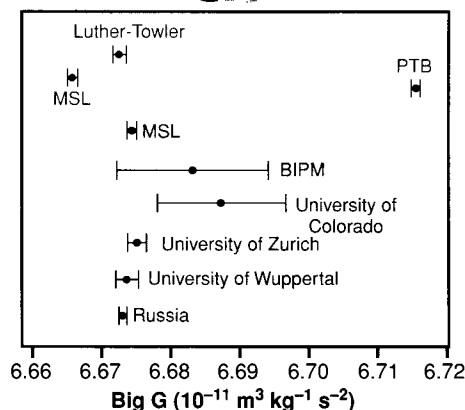
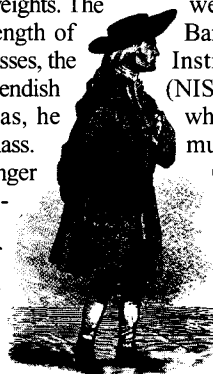
The mass of the Earth is no longer a burning question, but the Cavendish experiment is legendary. The torsion balance is still one of the best ways to measure gravity's strength, a number called the gravitational constant, or Big G.

G is perhaps the most elusive of all the fundamental quantities. While the charge of the electron is known to seven decimal places, physicists lose track of G after only the third. For some, that's an embarrassment. "It grates on me like a burr in the saddle," says Alvin Sanders, a physicist at the University of Virginia in Charlottesville.

Over the past few decades, he and a handful of other physicists have dedicated themselves to measuring G more accurately. To their dismay, they've come up with wildly different values. "You might say we've had negative progress," says

Barry Taylor, a physicist at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland. But when 45 members of the Big G community met last month* to honor the Cavendish anniversary and discuss the remarkable lack of progress over the last two centuries, they had a pleasant surprise. Six groups using a variety of techniques weighed in with new values of G, and they were all in rough agreement.

Because the results—one of which is reported on page 2230 of this issue—are preliminary and disagree with some older measurements, the G-men are cautious about declaring the case closed. But many suspect experimental finesse may finally be settling the long debate over the value of G. "The numbers are sort of converg-



Pulling together. New readings of G (red) are in rough agreement, hinting at an end to a quest that goes back to Henry Cavendish (top).

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