Organic Light Emitters Gain Longevity

Organic thin-film displays were for many years a research curiosity with no staying power. Now their stamina is beginning to match their unbeatable toughness and lightness.

The art of creating pure and precise films atom-by-atom is a key tool of the semiconductor industry. In this special issue, *Science* looks at new developments in thin-film technology. We begin with news reports on three younger fields that are being transformed by thin-film technology: organic films being put to use as displays and transistors; metallic multilayers and oxide films with bizarre magnetic properties; and thin-film superconductors. Articles from leading researchers in the field begin on p. 884.

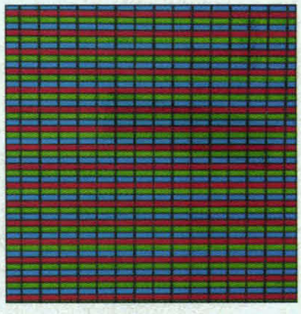
For much of the past decade, researchers have been promising to put thin films of light-emitting plastics and other organic materials on display: large, flexible, inexpensive and efficient screens to be used for everything from lightweight backlights for computer displays to TVs that you can hang flat on the wall or roll up and put in your pocket. Yet, many of these promises have fallen flat as well. Organic lights have tended to burn out after just days or weeks of operation. But now long-lived organic thin film displays are beginning to shine (also see Sheats *et al.*, p. 884).

By crafting films without as many burnout-causing defects and building devices with additional film layers to enhance light emission, researchers around the world have recently improved the brightness, the lifetime, and the future prospects of their devices. In May, for example, researchers at Kodak demonstrated organic light emitters that shine about half as bright as a fluorescent tube and last for 6000 continuous hours, which works out to the better part of a year. Japanese industrial giants Pioneer Electronic Corporation and Idemitsu Kosan also unveiled long-lived display prototypes this spring, which both companies say they'll have on the market next year.

"Whereas there was a great deal of skepticism a year ago that we could get long-lasting organic devices, we're now seeing you can get lifetimes of 10,000 hours or more," says Alan Heeger, a physicist at the University of California at Santa Barbara and chief scientist of Uniax, a high-tech start-up that's attempting to commercialize plastic-based displays and electronics. Ten thousand hours is more than enough lifetime for applications such as alphanumeric displays that are not on all the time, says Paul May, director of technology for Cambridge Display Technology (CDT) in the United Kingdom. "This field has moved from being a research curiosity to being a technology," he says. And recent advances are turning organic displays into "one of the hottest new areas in the display field," says Allan Kmetz, an optical physicist at Lucent Technology's Bell Laboratories (formerly AT&T Bell Labs) in Murray Hill, New Jersey.

Finessing films

At the heart of organic light-emitting devices (LEDs), which are the building blocks of these new displays, are thin films made from either small molecules—each of which is made up of a series of rings—or long chain-like polymers. To make an LED, one or more of these layers are sandwiched between two electrodes, one of which is transparent. When a voltage is applied between the electrodes, the electric field created pulls low-energy electrons from the organic material near the positively charged electrode, or anode. This leaves behind electron vacancies, dubbed holes, in the plastic. The negative electrode, or cathode, injects high-energy electrons into the adjacent material. The field makes these electrons and holes migrate toward each other through the film. When they meet in the middle, the energetic electrons can drop into the holes, giving up their excess energy as photons of light.



Glorious organocolor. Idemitsu Kosan's prototype thin-film organic display.

PHOTOS BY TADASHI KUSUMOTO/IDEMITSU KOSAN

Or at least they do in an ideal world. But in the real world, all too often electrons give up their excess energy as heat or molecular vibrations instead of light, which can cause either early burnout of the devices or a steady decline in brightness. Burnout frequently happens as a result of impurities such as tiny dust particles that get trapped in the film during growth, creating an overall unevenness in the film. When the voltage is applied, thinner regions of the film experience higher electric fields, creating hot spots that lead to fast burnout of those regions.

Dimming, meanwhile, often occurs due to irregularities in the pattern of organic molecules in the film that create "defects," which act as low-energy sites and can trap mobile electrons and holes as they move past. When they fall into such a trap, the electron or hole gives up a small fraction of its energy and no longer has enough energy to move. And even if they still manage to recombine with an oppositely charged partner, they typically have insufficient energy to produce a photon of visible light, and instead produce heat or vibrations. This unwanted energy dissipation not only lowers the light-emitting efficiency of the devices, says Uniax physicist Gang Yu, but it can also produce additional charge-trapping defects in the film, further dimming the device.

To slow this demise, researchers have hit upon several solutions: growing films with fewer impurities and charge-trapping defects to begin with; and altering the architecture of their devices and the chemical makeup of their materials to encourage more energy to be emitted as light instead of heat or lattice vibrations.

These strategies have worked particularly well for researchers developing small molecule–based organic LEDs, which now clearly have the endurance edge over their polymer rivals. Unlike polymers, small-molecule light-emitting films are grown as high-quality crystals, with all the molecules lined up in a repeated fashion. This regular arrangement is less prone to defects and misalignments, which makes it easier for charges to hop from one molecule to the next, says Ching Tang, a physical chemist at Eastman Kodak in Rochester, New York. To make their record long-lived LEDs, Tang and his colleagues improved the vacuum growth techniques they use to lay down ultrathin layers of organic light-emitters such as tris(8-quinolinolato) aluminum(III), or ALQ. The result was that the films in their new devices contain fewer impurities and charge-traps than previously, although Tang declines to offer additional details for proprietary reasons. Similar film

Plastic Transistors Gain Speed on Silicon

Displays are not the only organic electronic devices that have seen rapid improvements in recent months. While researchers have upped the brightness and lifetime of organic displays (see main text), they've also made significant jumps in producing high-speed transistors from thin-film organic plastics, which could be used for "smart cards" and other cheap throw-away memory devices, or in the array of switches that control the light emission from each picture element in conventional laptop computer displays.

First developed in the mid 1980s, organic transistors immediately raised the prospect of making displays and memory devices on cheap, flexible, and lightweight plastic instead of glass or silicon. But the devices have never really made it out of the lab, because the speed at which organic transistors can shuttle electronic charges—and therefore information—has consistently lagged behind that of amorphous, or non-crystalline, silicon, which is now commonly used in display circuitry and in other low-cost applications. Another strike against organic transistors is that they pass current even when turned off, a fault that virtually rules out use in laptop computer displays, where battery power is at a premium.

New research, however, has progressed on both of these fronts. At the Device Research Conference (DRC) in Santa Barbara in June, for instance, researchers at Pennsylvania State University in University Park unveiled thin-film transistors (TFTs) made from a crystalline organic film called pentacene that virtually match the speed and low-loss characteristics of amorphous silicon devices.

"I think it's a very positive result," says Christ Dimitrakopoulos, a materials scientist at IBM's T.J. Watson Research Center in Yorktown Heights, New York, who attended the DRC and has also worked on making pentacene-based transistors. But Dimitrakopoulos cautions that the new pentacene TFTs aren't ready for the market quite yet. Although the speed of charges and the amount of current leakage in the devices are "in the range where amorphous silicon works," says Dimitrakopoulos, he notes that the Penn State group's TFTs required voltages several times higher than those used to drive amorphous silicon transistors in conventional liquid crystal displays.

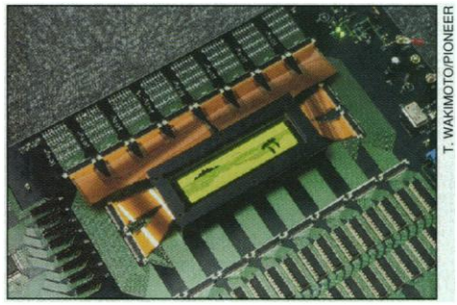
Still, the increased speed is impressive. Though Dimitrakopoulos and others have worked with pentacene for years, nobody has previously been able to coax charges to move through the material at a mobility greater than 0.08 centimeters^2 per volt-second, well below amorphous silicon's value of 0.5 to 1. But Tom Jackson, an electrical engineer who led the Penn State team, believes that's because the vacuum deposition techniques previously used to lay down the pentacene films did so too fast, which resulted in poorer-quality films riddled with unwanted charge-trapping defects. When Jackson and his colleagues slowed down their growth procedure to a crawl, they reduced the defects in their films and ultimately improved the charge mobility to between 0.6 and 0.7 cm^2/volt-second. Jackson's team also cut down on current drain by purifying the pentacene to sift out leakage-causing impurities.

In addition to the Penn State group, researchers at Bell Laboratories in New Jersey and the Laboratory of Molecular Materials of France's CNRS research agency in Thiais have also recently created TFTs based on other organic materials with mobilities greater than 0.1, which is considered the threshold for applications such as flat-panel displays or smart cards. Yet, according to CNRS chemist and physicist Francis Garnier, all of the new organic TFT materials still have an important drawback: they're not soluble in conventional organic solvents. That means that to coax the materials into films, researchers must use complex vacuum deposition systems rather than simply spin-coating them on a substrate like conventional plastic films. Finding ways to make high-quality films from cheap, soluble starting materials, says Garnier, "is the next very important goal." –R.F.S.

growth improvements have also helped lead to better small-molecule organic transistors (see box).

Another improvement, says Tang—whose team was the first to create light-emitters from organic thin films in 1987—was to add additional film layers to their devices to encourage charges to recombine near the center of the device. When electrons and holes combine near the edges of the film—at the interface between an electrode and the organic layer—they typically produce less light, since these regions are uneven and typically defect-rich. And since ALQ and other small-molecule light-emitters conduct electrons better than holes, the electrons get to one side quickly, causing just this sort of imbalance. To prevent this, Tang and his colleagues added another layer of organic molecules—such as N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, or TPD—between the light emitting–ALQ layer and the hole-injecting electrode. TPD and similar compounds conduct holes better than electrons, so its addition prevents electrons getting near the anode too soon, and gives the holes enough time to pass through this barrier to the ALQ, where they can then recombine with electrons to give off light.

A final improvement, says Tang, was to spike their ALQ layer with one of several beneficial impurities, known as dopants. Undoped ALQ devices have an initial brightness of about 510 candelas per square meter of surface (cd/m^2). Although the researchers do not yet fully understand the effect, they found that when they added a dopant called modified quinacridone (MQA) to their ALQ, the brightness jumped to 1400 cd/m^2, and the lifetime stretched to more than 6000 hours.



T. WAKIMOTO/PIONEER

Green screen. Pioneer's prototype has 16,000 elements and lasts 5000 hours.

Other teams have also taken advantage of the multilayer design. A group led by Takeo Wakimoto at Pioneer Electronic Corporation's Corporate R&D Laboratory in Saitama, Japan, unveiled a prototype bright-green organic display with over 16,000 individual LED picture elements and a lifetime of 5000 hours at a May conference of the Society for Information Display in San Diego, California. And at another conference that month, Tadashi Kusumoto and his colleagues at Idemitsu Kosan in Chiba, Japan, also described a prototype full-color organic display that uses a film of small organic molecules to generate blue light. To produce other colors, some of the picture elements are coated with fluorescent organic materials that absorb some of the blue photons, give up a small amount of energy, and then re-emit the rest as less energetic green or red photons.

Polymer progress

The success of small-molecule organic LEDs is turning some polymer-display researchers a bit green. "They're quite impressive," says

Heeger. "We have a bit of catching up to do," in achieving full-color and long-life devices, adds May. Although polymers may be lagging at the moment, if they can catch up on performance, May and others believe they will be unbeatable because of their flexibility and the fact that they should cost much less to make than crystalline films made from small molecules, which must be painstakingly grown in a vacuum. Polymer films, by contrast, can be made with lower-tech processing, such as spin-coating—put a drop of polymer solution in the middle of a substrate and spin.

And polymer LEDs are indeed making some headway in performance. At the Materials Research Society conference held in San Francisco last April, for example, Yu presented the latest work on Uniax's polymer devices showing a lifetime of over 10,000 hours at a brightness of 100 cd/m^2. Due to patenting concerns, Yu says that he cannot reveal the precise changes that led to the record-breaking lifetimes. He does say, however, that Uniax has been working to improve the contacts between the electrodes and polymers and refine the synthesis of their polymers to reduce the number of defect-causing impurities.

Other groups are also making progress. Emiel Staring's team at Philips Research Laboratories in Eindhoven, the Netherlands, recently announced polymer devices with lifetimes of several thousand hours. Meanwhile May and colleagues at CDT have created devices with modest brightness, but that last at least 7000 hours. Both Uniax and CDT officials say they hope to begin pilot production of devices next year.

Though some companies are pushing ahead with commercialization, they may have a tough time sorting out some of the fine details. Electrodes made from reactive metals like calcium are a particular problem. Such materials are unmatched in their ability to push electrons into organic films, boosting device brightness, but since these metals quickly degrade upon exposure to air or water vapor, commercial devices will have to be sealed tight against the elements. "I'm always concerned with technologies which depend for their life on good encapsulation, which is the case here," says Kmetz. Due to such concerns, Heeger says he expects that first-generation products are likely to be encased in glass. This will make the displays heavy and inflexible, thus losing some of benefits of using organic films. But now that organic light emitters are living longer, most display makers agree that companies now have an incentive to improve their encapsulation schemes. If successful, look out for an organic TV on a wall near you.

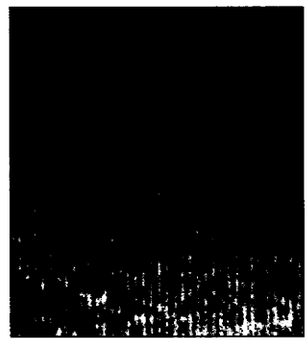
–Robert F. Service

MAGNETORESISTANCE

Multilayers and Perovskites Rewrite Rules of Resistance

In the 170 years since Georg Ohm identified a fundamental rule of electric current, his eponymous law has become almost as immutable as Newton's law of gravity: In a metallic conductor at normal temperatures, electric current is proportional to the applied voltage and inversely proportional to the metal's resistance. But 10 years ago, Peter Grünberg of the Jülich Research Center in Germany investigated a metallic structure that did not appear to obey Ohm's law. He constructed a sandwich of two iron layers separated by a thin film of chromium and found that at constant voltage he could vary the current through the sandwich simply by applying a magnetic field. The resistance of the structure could be changed with a magnetic field.

This phenomenon initially caused more curiosity than excitement, largely because the effect Grünberg produced was quite small. But 2 years later, when Albert Fert of the University of Paris Sud achieved a 50% change in resistance in a multilayer system of 40 layers of iron alternating with very thin films of chromium, several companies began to take notice. The phenomenon offered tantalizing prospects for applications such as reading heads in hard disk drives and digital videotape recorders: A device whose conductivity is exquisitely sensitive to magnetic changes would be ideally suited to quickly converting magnetically stored information into electrical signals.



C.H. CHEN & S.-W. CHEONG/BELL LABS, LUCENT TECHNOLOGIES

Deep freeze. Stripes of charge in manganese perovskite at 95 K.

These prospects spurred a frenzy of activity in labs around the world, and researchers were soon achieving huge changes in resistance in devices similar to Grünberg's. (Yvan Bryunseraede of the University of Leuven in Belgium holds the current record—a 220% resistance change—in a multilayer of 50 alternating films of iron and chromium, although he had to cool it to 1.5 kelvin.) The phenomenon has gained the title giant magnetoresistance (GMR), and the first GMR devices are "not so far off," says Grünberg. "We hold the basic patent for the application of GMR," he says, "and people at IBM, who have a license, say that around the turn of the century they expect to [have some products] on the market."

And these could be just the forerunners of devices based on an even more pronounced magnetoresistive phenomenon, dubbed colossal magnetoresistance (CMR). This new effect has its roots back in 1950, when two Dutch scientists, G. H. Jonker and J. H. Van Santen, of Philips in Eindhoven, who were studying complex oxide materials called manganese perovskites, noticed that these materials changed their resistance when they were placed in a magnetic field. Their results went largely unnoticed until 1993, however, when several groups—among them Fert's in Paris and teams at AT&T Bell Laboratories in Murray Hill, New Jersey, and the Max Planck Institute for Metals Research in Stuttgart—began working with these materials and soon reported changes in electrical resistance orders of magnitude greater than those achieved in GMR structures. "These materials ... really switch from metal to insulator in a field of a few tesla," says Andrew Millis of Bell Labs (now owned by Lucent Technologies).

Although the resistance changes in CMR materials are extreme, devices based on them may still be some way off because the effect is weaker at higher temperatures and can only be achieved at low temperatures and high magnetic fields. Nevertheless, research on these materials has skyrocketed worldwide, and it has benefited from the intense study of the closely related copper perovskites which were found to exhibit high-temperature superconductivity (HTS) in 1986. "People are using their experience [from HTS research]. This is why this area is evolving very rapidly," says Victor Moshchalkov of University of Leuven.

Many researchers believe that there are still more surprises in store from magnetoresistive materials. "People have not measured the magnetoresistance on many materials yet," notes Sungho Jin of Bell Laboratories, who coined the term CMR. Moshchalkov agrees, citing the unexpected discovery of HTS: "We know that oxides are insulators, and only a complete idiot would look for HTS in oxides. But these complete idiots were right."

Moment to moment. The key to GMR lies in the magnetic nature of the metals used in the multiple layers. Each atom in a metal can be viewed as a minute bar magnet: The electrons orbiting the nucleus create a tiny