Developments
in organic displays

by John K. Borchardt

Rapid advances in materials and manufacturing technology are making organic light-emitting diodes (OLEDs) the leading technology for a new generation of thinner, lighter, higher-resolution displays for computers, televisions, and small hand-held devices. In addition, OLEDs could enable the development of new display applications including flexible plastic display devices, displays embedded into clothes or wall hangings, and even head-mounted displays.

While current progress in OLED technology is rapid, its history begins more than forty years ago in 1963 when Pope and coworkers discovered electroluminescence in organic semiconductors[1]. The discovery excited little interest at the time, however, because of the high voltage needed and the short lifetime of prototype devices. This changed in 1987 when Tang and VanSlyke of Kodak reported efficient, low voltage electroluminescence in an organic thin-film device with a novel heterojunction structure[2]. Shortly afterwards, Friend and coworkers at the University of Cambridge created a similar device with a polymer, poly(p-phenylenevinylene), as the organic emitter[3]. Friend's innovation built on the discovery of conductive polymers by Heeger, MacDiarmid, and Shirakawa in the 1970s, which earned them the 2000 Nobel Prize in chemistry[4].

OLED technology is now being commercialized as a multi-billion dollar market. OLEDs are already used in small displays in cellular phones, car stereos, digital cameras, hand-held computer games, and other consumer devices such as electric razors and watches (Fig. 1). According to display industry analysis firm iSuppli/Stanford Resources, the global market for OLED displays will increase from $112 million in 2003 to $2.3 billion in 2008. In 2003, 17.3 million OLEDs were sold worldwide, and sales are expected to rise to 36.2 million units in 2004, reaching 366 million in 2010.

OLEDs offer several advantages over liquid crystal displays (LCDs) and the other technologies that currently dominate
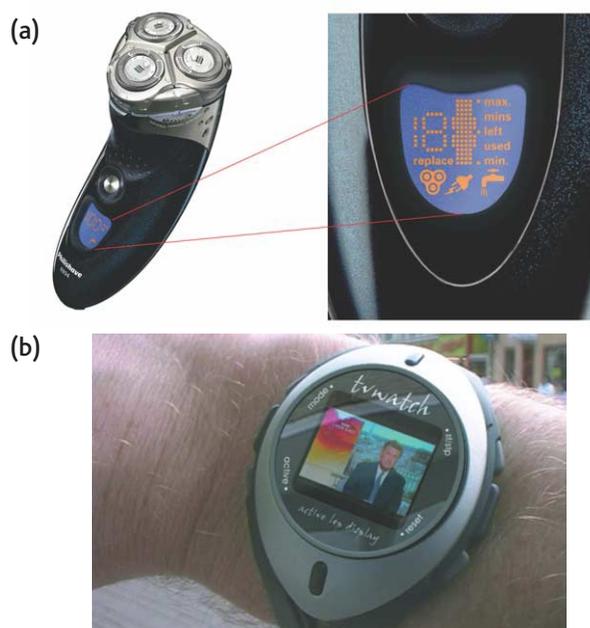
Fig. 1 (a) Norelco electric razor fitted with an OLED, which provides information on its operational status. (Courtesy of Philips.) (b) OLED watch face. (Courtesy of CDT.)

the global $31 billion flat-panel display market. Unlike LCDs, OLED displays do not require backlighting, so they can be thinner and lighter. In addition, because OLED panels emit light only from the necessary pixels rather than the entire panel, power consumption is 20-80% of that of LCDs. OLED displays also provide higher contrast and truer colors, higher brightness, wider viewing angles, better temperature tolerance, and faster response times than LCDs. The final, and perhaps most crucial advantage of OLEDs is that they can be deposited onto almost any substrate, both rigid and flexible, enabling a raft of new applications.

The rapidly growing market for OLED displays is driving research in both advanced materials and improved manufacturing processes. Since 1980, more than 6500 patents have been granted worldwide in this field, with activity accelerating since the late 1990s. Most of the major players in the area license OLED technology from either Kodak or Cambridge Display Technology (CDT), which was spun out of the University of Cambridge by Friend.

OLED anatomy

Fig. 2 illustrates the multilayered OLED structure that contains ultrathin electroluminescent organic films. These organic films are patterned into pixels that function similarly to standard LEDs. The usual structure consists of an anode, such as indium tin oxide (ITO), deposited onto a transparent substrate. This is followed by two conducting layers, a hole injection layer containing metal complexes based on Co(III) and Ga(III)[5] and an electron transport layer such as Al-poly(p-phenylenevinylene)[6], which sandwich the emissive organic layer. The structure is topped with a reflective metal cathode of Mg-Ag alloy or Li-Al. The thickness of these five layers is ~300 nm, but most of the weight and thickness of the OLED comes from the substrate.

When a voltage is applied across the electrodes, holes are injected from the anode and electrons from the cathode. The holes migrate through the hole injection layer, while the electrons migrate through the organic electron transport layer. The holes and electrons meet in the organic emitter layer where they recombine to form an exciton. Relaxation from the excited to ground states occurs, giving rise to light emission.

The organic emitter layer

The key material is that used in the organic emitter layer. This semiconducting organic layer must contain a material with conjugated π-bonds, but can be either a small molecule in a crystalline phase (small molecule OLEDs or SMOLEDs) or a polymer (polymer OLEDs or POLEDs). These molecules contain chemical groups called chromophores, which absorb incident energy and emit visible light. The color of the emitted light depends upon the precise composition of the material. Red, green, and blue emissive materials can be used together to produce the full color spectrum.

SMOLEDs use organic emissive materials with molecular weights up to several hundred daltons and do not contain repeating units as polymers do. Anthracene (three benzene
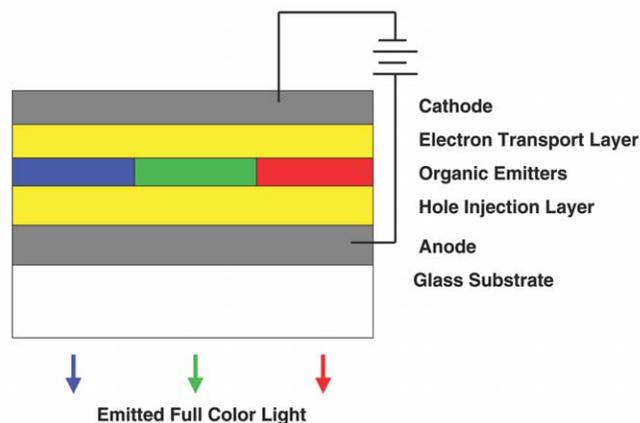

Fig. 2 Anatomy of an OLED.

rings fused in a chain) was the original material studied by Pope in his pioneering work on SMOLEDs[1]. Fused benzene ring compounds (arenes) are now commonly used and recently another promising class of arenes, pentacenes (chain-like structures of five aromatic rings), has been found[7]. Pioneered by Kodak, the technology has been licensed to IBM, UDX, and Ritek, who are now pursuing this approach.

Researchers are working to overcome the common limitations of SMOLED organic emitters, which include limited efficiency in converting electrical energy into light (electroluminescence efficiency), rapid degradation upon contact with oxygen or water (which makes production difficult), and poor solubility (which leads to aggregation). For example, many SMOLED organic emitters incorporate transition metal-atom-containing species that convert a high fraction of the input electric charge to emitted light[6,7]. Examples include adducts of the mercury trifunctional Lewis acid trimer and the arene compounds pyrene, naphthalene, and biphenyl. These adducts exhibit bright red, green, and blue phosphorescent emissions in the solid state at ambient temperatures[8-10]. These trimer-arene adducts overcome three limitations of SMOLED emitters:

- Typical arenes only fluoresce, limiting electroluminescence efficiency to 25%, while OLEDs containing phosphorescent trimer-arene adducts have an upper limit of 100%;
- Arene-arene intermolecular interactions in the solid state reduce device efficiency through self-quenching and excimer formation. These interactions are not present in trimer-arene adducts; and
- The trimer-arene adduct compounds provide better control of color than arenes alone.

Encapsulation technology is also being developed to reduce the degradation that limits SMOLED operating life, while reducing the undesirable effects of aggregation in the organic emitter. For example, poly(benzylaryl ether) dendrimers have been used to encapsulate quinacridone. Because dendrimers are soluble in organic solvents, spin-coating processes can be used[11]. However, the limited solubility of SMOLED organic emitter materials means devices cannot usually be fabricated using solution processing but require more expensive vacuum vapor deposition.

The alternative approach to small molecules is to use polymers as the organic emitter layer. CDT developed the POLED approach, which is also now being pursued by Philips, who have a number of products (Fig. 3), DuPont and its
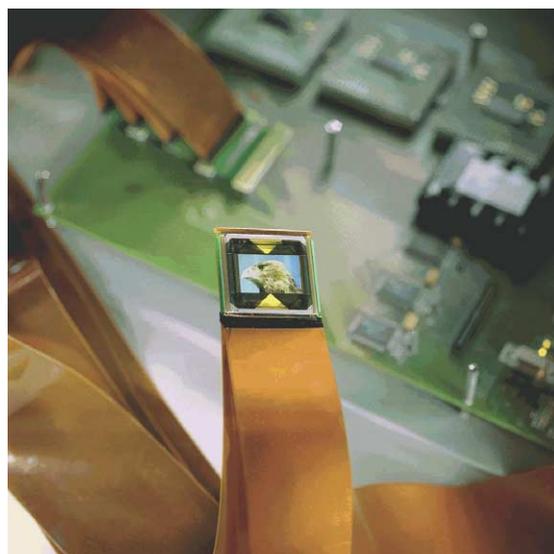

Fig. 3 Polymer OLED. (Courtesy of Philips.)

subsidiary Uniax, and Dow Chemical. POLEDs consist of a thin (0.1 μm) two-layer polymer film sandwiched between the two electrodes. The bilayer film consists of an emitting polymer layer, such as polyparaphenylene or polyfluorene, atop a conducting polymer layer, such as a combination of polyaniline and poly(styrenesulfonate) or poly(ethylenedioxythiophene) and poly(styrene sulfonate).

The combination of the electrical properties of metals and semiconductors with the mechanical properties of polymers enables POLEDs to be deposited on flexible substrates. Such flexible displays could find applications in portable computers, electronic books, and billboard-type displays. This is a unique advantage over both SMOLEDs and current display technologies. POLED displays also operate at a lower voltage and are more power-efficient than SMOLED displays. In addition to these advantages, manufacturing costs are lower because solution processing (spin coating) and ink-jet printing methods can be used instead of vacuum vapor deposition. However, there are important areas in which POLED technology needs improvement, including increased electroluminescence efficiency and longer operating life, particularly for blue light emitters.

Improving POLED efficiency

Until recently, it was thought that the light-emitting polymers used in POLEDs were inherently limited in efficiency, able to convert no more than 25% of their energy into light because of spin statistics. "We really need these
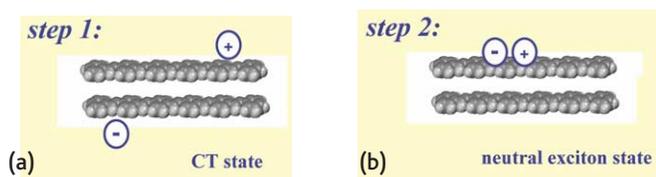
Fig. 4 (a) Step 1 of the proposed charge transfer mechanism. Formation of a loosely bound charge-transfer state. (b) Step 2 of the proposed charge transfer mechanism. Charge neutralization producing a singlet or triplet excited state (exciton). (Courtesy of Georgia Institute of Technology.)

polymers to go beyond 25% for the devices to be more efficient," says Jean-Luc Brédas of Georgia Institute of Technology. His theoretical studies indicate that higher efficiencies *are* possible[12,13].

Brédas proposes that the key to higher efficiency is the two-step charge recombination process that begins when initially separated charges combine to form a loosely bound charge-transfer state (Fig. 4a). When the opposite charges meet, they neutralize one another and produce a singlet or triplet excited state (exciton) (Fig. 4b). The decay of that excited state results in the emission of light. During the charge-recombination process, the spin directions of the electrons involved can orient themselves into four possible combinations, each with an equal statistical likelihood. The first pattern, a 'singlet', can have only one of the four possible spin combinations. The other, a 'triplet', can have three different combinations. Thus spin statistics predict that singlets will be formed in only 25% of charge recombinations, and only singlets produce light in π-conjugated polymers.

Brédas has shown theoretically that systems built from long polymer chains should be able to boost the percentage of light-emitting singlets to as high as 50%. This is because, with increasing molecular weight, triplets take longer to convert to neutral excitons. During this time, the triplet state can convert to a singlet, while singlet conversion to excitons remains rapid. As a result, spin statistics become biased in favor of singlet formation, which accounts for more than 25% of the four possible spin combinations. This results in an increase in POLED efficiency beyond the 25% limit. The π-conjugated polymer molecular weight required is still being defined, however.

"These results are important in the sense that they lead to an understanding of why polymer LEDs can have an efficiency that goes beyond the 25% limit predicted on the basis of simple spin statistics," says Brédas. Besides improving efficiency by using longer polymer backbones to increase molecular weight, Brédas is also investigating the use of

chemical group substituents on the polymer backbone to improve efficiency[11,12].

Eric Meulenkamp, principal scientist at Philips Research, has reported a different method of increasing POLED efficiency. By dispersing a phosphorescent 'guest' material into a light-emitting polymer 'host', it is possible to use all the excited states, both singlet and triplet, for light emission provided that the triplet energy gap of the host is higher than that of the guest[14]. Scientists at Philips Research and TNO Industrial Technology have developed a proprietary copolymer suitable for hosting a green triplet emitter and providing a high luminous efficacy of 24 cd/A. Still higher efficiencies and efficient blue emission could be achieved by further optimizing the copolymer composition.

Meulenkamp also reports increasing POLED efficiency using a proprietary anode layer[14]. The novel anode significantly reduces losses that arise from imbalances in the hole and electron partial currents. With present anode layers, the hole current can far exceed the electron current. This results in significant energy wastage, since the excess holes cannot combine with electrons to generate light. The new proprietary anode layer introduces a barrier to hole injection, thereby reducing the number of excess holes. With balance between holes and electrons at high voltage, efficiency is increased from 2-4% in conventional devices to around 12%. This translates into a luminous efficacy of 35 cd/A for a yellow light-emitting polymer and 20 cd/A for blue.

OLED display types

OLED displays can be either passive or active matrix. In passive-matrix display panels, the electrode material is deposited in a matrix of rows and columns. An OLED is formed at the intersection of each row and column. Display electronics can illuminate any OLED (pixel) in the array. A video image is created by sequentially scanning through all rows and columns, briefly switching on the pixels needed to display a particular image. An entire display screen is scanned (refreshed) in about 1/60 of a second. However, because of the high power consumption, passive-matrix displays can be made with only a limited number of pixels.

Active-matrix OLED displays are rapidly replacing passive-display OLED displays for full-color applications. Active-matrix OLEDs have an integrated electronic backplane as the substrate and are more suitable for high-resolution, high-information-content videos and graphics. However, they are

significantly more expensive than passive OLED displays. In an active-matrix display, the array is still divided into a series of rows and columns, with a pixel formed at the intersection of each row and column. However, each pixel now consists of an OLED in series with a thin-film transistor (TFT). The TFT is typically low-temperature polycrystalline Si (LTPS) and controls the amount of current flowing through the OLED. LTPS transistors have high current carrying capacity and high switching speed. The TFT in each pixel controls the brightness and the current flowing through the OLED. This continuous operation eliminates the need for the very high currents required in passive-matrix OLED displays. Resolution can be increased using single-crystal Si substrates instead of LTPS.

The future

Continued improvements in advanced materials will enable OLED display manufacturers to enhance lifetime, stability, and light efficiency. Efforts are also under way to reduce the negative effects of heat, moisture, and dust on OLED performance, while maintaining the advantages of low weight and thin profile.

Improved manufacturing processes are being developed to overcome the difficulty of forming organic layers on large-sized TFT substrates. For example, Seiko Epson has used its proprietary ink-jet printing technology to form organic layers on large TFT substrates. The result is the largest OLED display to date, a 40-inch full-color (260 000 colors) prototype. The same technology could also lower the manufacturing costs of smaller OLED displays if they could be cut from larger TFT substrates after deposition of the organic layer. David Fyfe, chief executive officer of CDT, forecasts that when sufficient OLED production volume is achieved, prices should drop to 10-40% less than LCDs.

According to Kimberly Allen, director of technology and strategic research at iSuppli/Stanford Resources, it is too soon to say whether SMOLED or POLED technology will dominate. "Polymers may be better suited for large area manufacturing applications," Allen notes. "On the other hand, small molecules may be better at high-resolution applications."

Universal Display Corporation's (UDC) vice president of technology commercialization, Janice Mahon, suggests that the distinctions between SMOLEDs and POLEDs will matter less in the future. For example, researchers at Covion Organic Semiconductors are developing hybrid active-matrix OLEDs with small-molecule-doped polymer systems. The goal is to combine the easy processing of light-emitting polymers with the high luminescence efficiency of small molecules. UDC is using a laser-induced thermal imaging process to create stripes of small molecules and polymers in a multi-layered structure for the organic emitter layer[15].

Meanwhile, UDC and DuPont Displays are collaborating to combine the best qualities of their distinctly different approaches: UDC's high efficiency POLEDs and DuPont's solution-based manufacturing processes. CDT is also developing a hybrid system based on light-emitting polymers and dendrimers, which combines the advantages of small molecules (high efficiency) with polymers (less expensive to manufacture). However, OLEDs based on dendrimers alone have insufficient service life for commercialization.

Continued development of flexible plastic displays and organic electronics will play a key role in OLED development and commercialization over the next decade, according to iSuppli/Stanford Resources. With more than 80 companies and universities around the world working on OLED technology, future advances seem certain. **MT**

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