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Establishing the Operational Durability of Polymer Light-Emitting Diodes

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Abstract

This is the final report of a two-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). Recent research has made it clear that polymer light-emitting diodes (PLEDs) have all the necessary device attributes (efficiency, emission colors, operating voltage) required to build a successful display technology. This project was initiated to establish meaningful device operating lifetimes and to understand PLED failure mechanisms in order to control device reliability and ultimately produce a viable commercial product. A PLED lifetime testing capability was established to measure the change in PLED light output and drive voltage at constant current bias as a function of time for different current bias levels, operating temperatures and device (polymer) thicknesses. The dominant failure mechanism of the polymer light emitting diodes, occurring at less than 1000 hours of operation, was identified as delamination of the electron-injecting metal contact. A new electroabsorption technique to measure the electric field distribution inside the PLEDs was developed and then used to assess relative device reliability.

Background and Research Objectives

Recently, scientists at the Cavendish Laboratory in Cambridge, England discovered that sandwiching the polymer poly(*p*-phenylene vinylene) between a pair of appropriately chosen metal electrodes and applying a bias voltage can result in the emission of light. Since this important work, electroluminescence from a number of different semiconducting polymers with colors ranging from red to blue has been reported. These polymer light emitting diodes are now comparable in brightness to conventional red LEDs. Still, PLEDs remain an essentially new, uncertain, and relatively unexplored alternative to liquid crystals for display technology. At this early stage in the development of PLEDs, the risk

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associated with the uncertainties in stability, lifetime, and other characteristics is too high to motivate the private sector to dedicate sufficient resources for an aggressive development program. Yet the potential economic rewards of such a program are considerable. Successful creation of a strong proprietary position and an accompanying manufacturing technology could, by relatively conservative estimates, lead to the establishment of a completely new, billion dollar US industry by the end of the decade.

To meet the challenges faced by PLED technology, Los Alamos National Laboratory (LANL) started a Laboratory Directed Research and Development (LDRD) project to investigate PLEDs for display and optical communication applications. Since the beginning of this project we have established collaborations with Hewlett-Packard, Uniax, the University of Texas at Dallas and the University of California at Santa Barbara. The Los Alamos effort consists of both experimental and theoretical efforts working in close collaboration. Experimentally, polymer films and devices are fabricated and studied using a variety of optical spectroscopies, electrical transport and device measurements. Theoretical investigations are being conducted at both the molecular and the device levels.

Although there is moderate risk that polymer light emitting diodes will never become sufficiently competitive to displace current technologies, successful completion of this project will enjoy considerable economic and technical leverage. From an economic standpoint, the portion of the display market that PLEDs could capture is substantial. Consider, for example, the case of alphanumeric character strings. For short character strings, inorganic LED technology is now frequently used. However, such displays are relatively expensive to manufacture, since they involve individually connecting hundreds of LEDs into a package. In contrast, a display made with PLEDs would be far cheaper to make, and could easily be extended to much longer character strings. The two lists of steps below describe both the fabrication sequence used to make conventional LED alphanumerics and the simple process that might be used for polymer displays. This comparison illustrates that polymer displays could be significantly easier to fabricate than conventional LED alphanumerics.

Alphanumeric Display—Processing Sequence

Conventional LED

Grow GaAs or GaP ingot
Prepare polished wafers
Epitaxial semiconductor growth
LED wafer processing
Dice wafer into individual LEDs
Test LEDs
Prepare substrate/pc board
Pick/place/attach individual LEDs
Wire bond LEDs to pc board
Encapsulate

Polymer LED

Prepare substrate/pc board
Spin-on polymer
Pattern metallization over
polymer and pc board
Encapsulate

Even more substantial economic leverage is possible in the area of higher information content displays where liquid crystal flat panel displays (FPDs) currently dominate. This market is in its rapid growth phase. At present, the lead in the global race to develop this technology clearly goes to the enormous effort on active and passive matrix liquid crystal displays (LCDs) in Japan. However, the LCD display fabrication process is inherently difficult (complicated processing, low yields, low light throughput, high cost, etc.), which limits both its present applications and its future use in high-definition displays. Any competing technology that resolves many (or all) of these difficulties could gain a significant share of the FPD market.

The operating lifetime of PLEDs is the most critical issue limiting their commercialization. To date there has been no systematic study of their operating lifetime or of the failure mechanisms of these devices. The dependence of the lifetime on operating conditions such as current bias and temperature, and device parameters, such as thickness of the polymer film, has not been investigated. There is anecdotal evidence that long lifetimes can be achieved. These results are encouraging and suggest that there are as yet unknown parameters in the device processing which, if properly controlled, can lead to durable devices.

Importance to LANL's Science and Technology Base and National R&D Needs

Organic electronic materials have the potential to revolutionize key technological areas including information display and optical communication. Major advantages of organic materials are their ability to be processed economically in large areas, the tunability of their electronic properties, and flexibility in materials design. The use of organic materials for electronic applications is a new and rapidly developing field in which increased understanding can have major technological and scientific impact. Polymer LEDs are by far the most important organic electronic devices that are currently under investigation. If polymer LEDs become part of a successful technology, further research on organic electronic materials will be stimulated. This LDRD project helps to establish a leadership position for Los Alamos in the emerging area of organic electronics by demonstrating that organic electronic materials are commercially viable.

In addition to their use in flat panel displays, polymer LEDs have the potential to be the key element in optical interconnects for conventional silicon integrated circuits. If this capability can be realized, it will have a tremendous impact on the architecture and performance of complex computing and communication systems. The current metal-line interconnect technology has severe limitations for complex, high-speed systems. The line capacitance loads the circuits, slowing them down and the lines must be spaced sufficiently far apart to avoid crosstalk. Using PLEDs an integrated, all polymer, high-speed optical communication system that avoids both of these problems can be realized.

An integrated optical interconnect technology would be immediately valuable to the Accelerated Strategic Computing Initiative (ASCI). It would enable the development of extremely high speed, digital signal processing and computing techniques that are critical to the economic and military security of the United States. The US is rapidly losing its lead in integrated circuits and advanced computing. Integrated optical data transfer could lead to a substantial improvement in signal processing and computing power. This could help reestablish US leadership in advanced data processing.

The flat panel display market was approximately \$9B in 1994 and it continues to grow rapidly. Liquid crystal display technology, which dominates the flat panel display market with an 85% share, is controlled by Japanese companies. Despite extremely large investments, this is still a limited technology and a fundamentally new approach based on polymer LEDs is capable of capturing a significant share of the market. Polymer light emitting diodes are attractive as an alternative display technology because they are highly efficient, their emission spectrum can be tailored to span the visible spectrum and they can

be processed in large areas at low cost. Although difficult to estimate, polymer LEDs could reasonably be expected to capture 10% of the flat panel display market over the next five years, corresponding to a market in excess of \$1B. Ultimately, PLEDs have the potential to dominate display technology.

Today, Japan dominates the global display market. One estimate by the Department of Energy puts the Japanese share at 98% and the US share at < 2%. A major change in this unfavorable position is needed. Display technology is an essential component of all advanced military and defense systems. PLEDs have the potential to displace LCD and cathode-ray-tube displays presently used in military, high information content displays. The US is in a strong position to become a major manufacturer of PLED-based displays because of aggressive involvement by US companies, notably Hewlett-Packard. Establishing a strong US manufacturing base in PLED display technology would free the US from its debilitating reliability on Japan for display technology.

Scientific Approach and Accomplishments

The principal goals of our work during this period were to set up a PLED lifetime testing capability, to establish a base line of information on PLED lifetimes and to understand the failure mechanisms involved. There are two basic types of PLED structures which are shown in Fig. 1: simple metal-polymer-metal structures and more complex double heterostructure PLEDs.

The metal-polymer-metal structure consists of an electron injecting contact, the polymer active layer and a hole injecting contact on a glass substrate. The electron injecting contact is typically a low work function metal such as calcium or aluminum and is a few hundred nm thick. The polymer active layer is a conjugated polymer such as polyphenylene vinylene (PPV) that is between 50 and 200 nm thick. The hole injecting contact is typically a high work function metal such as gold or indium tin oxide which is made thin enough to be highly transparent in the visible spectrum. The double heterostructure device is similar except that the polymer layer is surrounded by two additional layers, an electron transport layer (ETL) and a hole transport layer (HTL), both typically 50 nm thick. The electron transport layer is used to transport electrons and block the transport of holes; similarly, the hole transport layer is used to transport holes and block the transport of electrons. This double heterostructure confines the electrons and holes in the polymer and enhances the device efficiency.

To establish a base line of information on PLED lifetimes we measured the change in PLED light output and voltage at constant current bias as a function of time for different current bias levels, operating temperatures and device (polymer) thicknesses. Current bias was varied between 0.001 A/cm^2 and 1 A/cm^2 , operating temperatures between -40° and 100° C were investigated, and device thicknesses between about 50 nm and 200 nm were considered. Devices were fabricated on 2-inch sapphire substrates to ensure good thermal contact between the PLEDs and the heater/cooler unit in the test station. Twenty five devices, each 2.5-mm in diameter, will be fabricated on each substrate. A simplified schematic diagram of the test station layout is shown in Fig. 2. The test station consists of a vacuum chamber with an optical window, a heater/cooler unit and five banks of five current sources (i.e., the 25 devices were divided into 5 groups of 5 devices; the 5 devices in each group will always be tested under the same current bias but the bias of the 5 groups can be separately varied). The electroluminescence intensity of the devices under test was monitored with a charge coupled device (CCD) camera.

In order to discover the failure mechanisms of the PLEDs, a set of postmortem experiments examined in more detail specific devices after the stress of the lifetime test. We measured the electrical properties, such as current-voltage (IV), capacitance-voltage (CV) and light-current (LI) curves, of selected devices. Optical microscopy was used to determine the spatial distribution of luminescence before and after stress, which provided some insight into local imperfections. Electroabsorption measurements were used to measure electric fields within the PLED. Information obtained from these detailed measurements was used to formulate both chemical/microstructural and device models of the PLEDs.

The primary results of this work are a detailed understanding of the device physics governing the operation and failure of the PLEDs and insight into the microstructural properties of the polymer active layer as described in the publications listed below. The dominant failure mechanism of the polymer light emitting diodes, occurring at less than 1000 hours of operation, was identified as delamination of the electron injecting metal contact. A new electroabsorption technique to measure the electric field distribution inside the PLEDs was invented and then used to assess relative device reliability.

Publications

1. Campbell, I. H., Ferraris, J. P., Hagler, T. W., Joswick, M. D., Parker, I. D., and Smith, D. L., "Measuring Internal Electric Fields in Organic Electronic Devices Using Electroabsorption Spectroscopy," *Polymers for Advanced Technologies*, (accepted for publication).
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3. Joswick, M. D., Campbell, I. H., Barashkov, N. N., and Ferraris, J. P., "Systematic Investigation of the Effects of Organic Film Structure on Light Emitting Diode Performance," *Journal of Applied Physics*, **80**, 2883 (1996).

PLED Device Structures

Figure 1. Schematic diagram of the two basic PLED device structures we investigated. The metal-polymer-metal structure consists of an electron-injecting contact (Ca), the polymer active layer (PPV) and a hole-injecting contact (Au) on a glass substrate. The double heterostructure device is similar except that the polymer layer is surrounded by two additional layers, an electron transport layer (ETL) and a hole transport layer (HTL).

Schematic Diagram of PLED Lifetime Test Station

Figure 2. Schematic diagram of PLED lifetime test station. The PLEDs in the test station are biased by a constant current source and the emitted light was collected by a lens and focused onto a CCD camera.