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Polymers for Integrated Optical Interconnects

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Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The recent discovery of electroluminescent polymers opens up, for the first time, the possibility of using optical interconnects for conventional silicon integrated circuits (ICs). If this capability can be realized, it will have a tremendous impact on the architecture and performance of complex computing and communication systems. The primary objective of this project was to understand the light-emission mechanism of electroluminescent polymers and to use this knowledge to make efficient light-emitting-polymer diodes (LEPDs). These devices are the critical missing element for a polymer-based integrated-optical interconnect technology. We studied and obtained experimental results in several areas including the energetic position of fundamental excitation, the degradation of the polymer caused by oxygen, and the luminescence efficiency of polymer and oligomers. Parallel to the experimental effort, theoretical calculations were performed on the microscopic scale and on the device scale.

1. Background and Research Objectives

Five years ago scientists at the Cavendish Laboratory in Cambridge, England demonstrated that light emission from the polymer poly(*p*-phenylene vinylene) can be stimulated by sandwiching it between a pair of appropriately chosen metal electrodes and applying a bias voltage. Although the first polymer light emitting diodes (PLEDs) required large drive voltages (~20 V) and were less than one percent efficient, their discovery made it possible, for the first time, to seriously investigate the use of optical interconnects for conventional silicon integrated circuits. If this capability can be

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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 cross-talk. As shown schematically in Fig. 1, semiconductor circuit designers have long dreamed of connecting integrated circuits optically.

Conceptually, a polymer-based optical interconnect is ideal. Polymers can be readily applied to the surface of an IC without degrading the performance of the underlying circuit. Polymers also conform easily to the topography of an IC or to the gaps between ICs. The main problem has been the lack of an integrable light source. Discrete light-emitting diodes could be attached to an integrated circuit by hybrid circuit techniques, but for interconnection of complex circuits this is completely impractical. Polymer light emitting diodes promise to be a cost effective, integrable light source. Because PLEDs are the critical component of this optical interconnect technology, we have concentrated our effort on understanding and developing PLED technology.

Since this project began, there have been significant improvements in PLED performance. Light output efficiency has been increased by more than one order of magnitude, resulting in PLEDs comparable in brightness to conventional red light-emitting diodes (LEDs). A number of important device characteristics have also been demonstrated, such as operating voltages of order 5 V, colors throughout the visible spectrum, and simple methods of device fabrication (processing the luminescent materials from solution).

Although dramatic progress has been made, there are a large number of scientific and technical issues that need to be addressed in order to continue the development of PLED technology. For example, PLED efficiency needs to be improved to minimize power dissipation and improve device lifetime, and the physical mechanisms responsible for charge injection and radiative recombination in the diode structures need to be understood in order to design new polymer materials with improved properties.

Our project involved a unique combination of experimental and theoretical researchers working together to solve these problems. The startling success that has already occurred in this field is likely to continue as we improve our understanding and control of PLEDs.

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

The development of extremely high-speed digital-signal processing and computing techniques is critical to the economic and military security of the United States. At Los Alamos, an optical interconnect technology is of value in the verification programs. It could provide a compatible interconnect overlay for high-speed microelectronic and optoelectronic devices. The immunity to electromagnetic interference and the high data rates are both potentially important to this program. In addition, the proposed study is complementary to the LANL super-computing initiative as well as to the proposed Laboratory thrust in nanotechnology and molecular electronics.

3. Scientific Approach and Results

Polymer light emitting diodes consist of a thin polymer film sandwiched between high- and low-work-function metals. The diode is biased so that electrons are injected from the low-work-function metal and holes are injected from the high-work-function metal. The electrons and holes recombine in the polymer, resulting in the emission of light. In order to design device structures, it is necessary to understand the injection process at the metal-polymer contacts, and the electric field profile and the distribution of charged carriers in the device. We wish to obtain information on effective Schottky barriers and charged-carrier trapping sites which influence these processes.

The primary polymer materials we studied are poly(p-phenylene vinylene) (PPV) and soluble derivatives of PPV. In addition to changing the solubility of the polymer, the addition of side groups to PPV changes the energy gap. The energy gaps of these PPV-based materials are: 2.4 eV (PPV), 2.25 eV (BCH A-PPV) and 2.1 eV (MEH-PPV).

We studied and obtained results in a wide spectrum of problems, such as the energetic position of fundamental excitation, the degradation of the polymer caused by oxygen, and the luminescence efficiency of polymer and oligomers. Parallel to the experimental effort, theoretical calculations were performed on the microscopic scale and on the device scale.

Internal photoemission measurements on a series of metal-MEH-PPV-metal structures were performed. The structures were designed so that the internal

photoemission signal originates from the Schottky barrier of only one of the metal contacts. We obtained good agreement with the ideal Schottky barrier model for metals with work functions from 3 eV to 5 eV. By varying the dc bias on a single structure, we also measured the electron and hole Schottky barrier heights of the same metal contact, thereby obtaining the energy separation of the intrinsic excitations of the polymer.

Photothermal deflection spectroscopy (PDS), optical absorption, and time-resolved photoluminescence were used to characterize the effect of photo-oxidation of MEH-PPV. A spin-cast polymer film was exposed to oxygen and to above-band-gap light (490 nm) up to 3.6 J/cm^2 . With increased illumination dose, several effects could be seen: the time constant of the initial, fast component of the photoluminescence decay became shorter; the intensity of the 0-phonon line in photoluminescence (PL) dropped rapidly; the peak in PL and in optical absorption showed a blue shift; and the principal absorption decreased in intensity. This decrease in absorption was much less pronounced than the decrease in PL intensity. In addition, a long tail in the absorption can be seen in the PDS spectra, extending from 1.0 eV to 2.0 eV. The intensity of this absorption tail increased with increasing dose of illumination.

We explain the experimental results with a breaking of the vinyl linkage in the polymer chain and a simultaneous built-up of carbonyl groups. These carbonyl groups create quenching centers which act as traps for the charge carriers. Breaking the vinyl bond shortens the conjugation length, which explains the blue shift in the spectra.

High photoluminescence efficiencies are desired to increase the brightness and operating lifetimes of organic light-emitting diodes. We performed transient PL-decay of PPV-type oligomers composed of three to five phenylene rings in blends and as pure films. The variation of the PL-decay with temperature, emission energy, and excitation energy were studied, and the changes in lifetime were correlated with the changes in relative efficiency. The results were compared with those of thin films of PPV. As can be seen in Fig. 2, the temperature dependence of the oligomer blends is smaller than in the case of polymer films. In the oligomer blends, the PL spectrum changes with excitation energy and emission energy, indicating an inhomogeneous distribution of molecular sites.

We believe that the temperature-dependent photoluminescence quenching in the studied PPV-type materials is dominated by migration of excitons to quenching centers. Chemical defects like carbonyl groups may play a role. In our simple model the excitons experience ultrafast vibrational relaxation and migrate to lower-energy sites

before they decay radiatively. A significant fraction of them gets trapped at quenching centers where they experience radiative and nonradiative recombination with an effective decay time of $1/t = 1/t_r + 1/t_{nr}$. Low temperatures favor the radiative channel which indicates that the migration and/or the trapping is temperature activated. In dilute systems the quantum efficiencies are much higher and the temperature dependence is weak. Spin-cast films of conjugated polymers contain high densities of conformational defects that make their absorption spectra look like a sum of medium-length oligomers. The large shift seen in the PL spectra of oligomer blends at low temperatures upon excitation at different wavelengths demonstrates inhomogeneity even in the case of short and chemically identical molecules. This is related to the high number of possible conformations (e.g. cisoid linkages, dihedral angle) and varying guest-host interactions.

In our theoretical effort, we have described a device model for PLEDs based on the nondegenerate Brazovskii-Kirova (BK) model for the electronic structure of polymers. Polarons and bipolarons are the principal charged excitations in the BK model. Polarons are singly charged excitations and play the primary role in charge injection and experiments such as internal photoemission that probe single-particle properties. The effective Schottky barrier at a metal/polymer interface is the energy difference between the Fermi level and the polaron energy after any region of rapid "band bending." Bipolarons are doubly charged excitations that can play an important role in establishing effective Schottky barriers at metal/polymer interfaces. The Schottky barriers are determined by the relative energy positions of the metal chemical potential and the polaron and bipolaron formation energies per particle. For the density of traps and device thicknesses that we considered (a range corresponding to that occurring in typical PLEDs), the PLEDs are fully depleted. The maximum built-in potential in a PLED device structure is the difference in formation energies per particle for negative and positive bipolarons. Changes in capacitance with bias voltage are determined by traps unless the trap density is less than about 10^{16} cm^{-3} . An example of the calculated electric field and the charge carrier density is shown in Fig. 3.

This device model is useful in the interpretation of three kinds of experiments: capacitance-voltage measurements, electroabsorption measurements to determine the built-in potential in PLEDs, and photoemission measurements to measure Schottky barriers at metal/polymer interfaces.

Capacitance-voltage measurements on PLEDs fabricated using MEH-PPV have shown that the devices are fully depleted and the trap densities are of the order of

a few 10^{16} cm^{-3} or less. Electroabsorption measurements show that the built-in potential in PLEDs scales with the work function difference of the contacts over a range of work functions, but saturates when the work function of one of the metal contacts is out side of that range. Internal photoemission measurements show that the effective single-particle energy gap is somewhat larger than the saturated built-in potential determined from the electroabsorption measurements and gives values for the effective Schottky barriers that are consistent with these measurements. Taken together, the results of these measurements support the model presented here.

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Fig. 1. Integrated optical interconnects between integrated circuits.

Fig. 2. Integrated PL intensity vs. temperature for oligomer blend, MEH-PPV, pure oligomer and PPV. The intensities are normalized to the estimated value at 0 Kelvin.

Fig. 3. Energy diagram (upper panel) and charge density (lower panel) at a forward bias of 1.0 V, with the chemical potential of the left (right) contact of 1.2 V (-1.2 V). A uniform density of $5 \times 10^{16} \text{ cm}^{-3}$ traps of each charge sign is included. The negative (positive) trap energy is 0.6 eV (-0.6 eV).