

Nanosecond transient electroluminescence from polymer light-emitting diodes

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The transient electroluminescence from polymer light-emitting diodes is reported. When the devices are mounted on a microstrip transmission line, the temporal response is limited by the electrode geometry, with rise and fall times below 50 ns. With low duty-cycle pulses (0.5%) the electroluminescence intensity remains proportional to the current at values up to 10 A/cm^2 , two orders of magnitude greater than possible under direct current operation. Since the spectral blue-shift observed at high current levels (with power dissipation above 1 W/cm^2) indicates significant sample heating, still higher levels should be possible with proper thermal management.

Initial results from semiconducting polymers employed in light-emitting diodes (LEDs) have demonstrated various colors (red, yellow, green, and blue) with impressive efficiency, brightness, and uniformity.¹⁻⁷ Flexible light-emitting structures, which take unique advantage of the processing advantages and mechanical properties of polymers, have been fabricated.⁸

Although the initial characterization of the polymer LED devices emphasized direct current (dc) characteristics, pulsed excitation provides important new information: the transient on/off response will ultimately limit the high-frequency modulation of such light sources, and the extension of the light intensity vs current characteristics to high injection levels will determine the potential of polymer LEDs in applications which require multiplexing (e.g., displays) or which require high levels of pumping (e.g., diode lasers).

This letter reports the transient electroluminescence (EL) from polymer light-emitting diodes, including measurements of rise and fall times, pulsed light intensity vs current, and pulsed emission spectra. When the devices are mounted on a microstrip transmission line,⁹ RC limited response is observed, with rise and fall times below 50 ns. With low duty-cycle pulses (0.5%), the EL intensity remains proportional to the current up to 10 A/cm^2 , two orders of magnitude greater than possible under direct current operation. The emission spectrum is blue-shifted at high current levels ($>1 \text{ W/cm}^2$) indicating significant sample heating. Thus, proper heat sinking should make possible still higher levels.

The device geometry is displayed in Fig. 1. The light-emitting diodes consist of an electron-injecting metal contact on the front surface of a poly [2-methoxy,5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] [MEH-PPV] film on a glass substrate; the latter is partially coated with an indium-tin oxide [ITO] electrode as the hole-injecting contact.⁷ The MEH-PPV films are prepared by spin-casting from xylene solutions containing 0.5% MEH-PPV by weight. Metal contacts (250 Å of calcium followed by 1200 Å of aluminum) are deposited on top of the polymer films

by vacuum evaporation at pressures below 10^{-6} Torr. All processing steps are carried out in a nitrogen atmosphere.

For the transient experiments reported in this letter, the low capacitance devices had active areas of $4 \times 10^{-3} \text{ cm}^2$. Transient measurements of larger area devices with dc characteristics as previously reported⁷ indicate that the devices turn on with rise times of a few μs , a speed which agrees reasonably well with the RC time constant of $RC=2 \mu\text{s}$ ($R=1 \text{ k}\Omega$ and $C=2 \text{ nF}$ measured at 100 kHz with a Hewlett-Packard 4192A impedance analyzer). In order to improve the frequency response of the devices, smaller area LEDs were prepared and mounted onto a microstrip transmission line.⁹ Indium solder is used to make contact between the device electrodes and the gold microstrip line. This design ensures that circuit elements external to the LED do not limit device response. The measurements are carried out at room temperature with the LEDs in a vacuum cryostat at pressures below 10^{-4} Torr.

For transient electroluminescence (EL) measurements, $1 \mu\text{s}$ voltage pulses (with 9 ns rise and fall times, 90% to 10%) from a Hewlett-Packard 214 pulse generator are applied to the device, and the emitted light is collected by a photomultiplier tube (Hamamatsu R928 PMT). The pulse shape and the PMT signal are recorded and averaged by a box car signal processor (EG&G 4402) with 2-ns gate width.

The EL decay plotted in Fig. 2 occurs on the falling edge of an applied 40-V pulse. The characteristic fall time (90% to 10%) of the electroluminescence is about 40 ns. Although the 40-ns characteristic time is in agreement

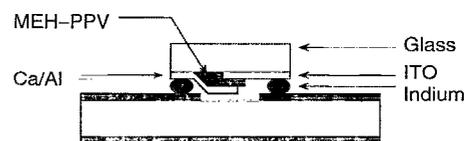


FIG. 1. Side view of the device geometry as mounted on the microstrip line.

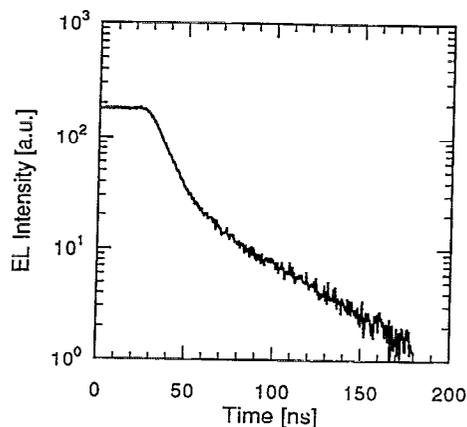


FIG. 2. Decay of luminescence intensity following the falling edge of an applied square voltage pulse.

with that expected from the RC time constant ($C=48.8$ pF and $R=810$ Ω as measured at 100 kHz; $RC \approx 40$ ns), the decay is nonexponential; it can be described as the sum of two exponential decays with time constants of approximately 11 and 60 ns, respectively. Rise times (10% to 90%) occur approximately as fast; e.g., the leading edge of the above pulse resulted in an EL rise time of 50 ns. The initial decay of the luminescence may actually occur faster than the 11-ns time constant, because that value is comparable to the response time of the PMT detector.

If the RC time constant could be reduced to values below the characteristic emission times of the electroluminescence, such transient measurements could provide fundamental information on the time scales for transport and/or emission processes. From a nonpolymeric organic EL layer, Hosokawa *et al.* report an EL response time of 100 ns in devices having a RC time constant of 5 ns.¹⁰ The corresponding photoluminescence lifetime is 16 ns, so it is possible for them to record carrier transit times and infer mobility.

Radiative recombination in *p*-phenylene vinylene has been observed in photoluminescence experiments with characteristic decay times of several hundred picoseconds.¹¹ This time scale is confirmed in MEH-PPV by work in progress in this laboratory. In order to observe such intrinsic features in EL behavior would require a device geometry with RC response faster than the photoluminescence decay.

Viewing the device with an equivalent circuit model provides a rough guideline of how to improve device performance. In such a model, the LED is represented as a capacitor with a parallel resistance the magnitude of which is determined by the bulk resistivity of the semiconducting polymer; this parallel RC is in series with an external resistor, R_s . Use of lower resistance electrodes and low resistance hole and electron transport layers would reduce R_s .^{2,12} Smaller area devices can be fabricated with lower capacitance. These can both be accomplished, in principle, while also increasing the parallel internal resistance (R_p) of the luminescent polymer through use of higher purity

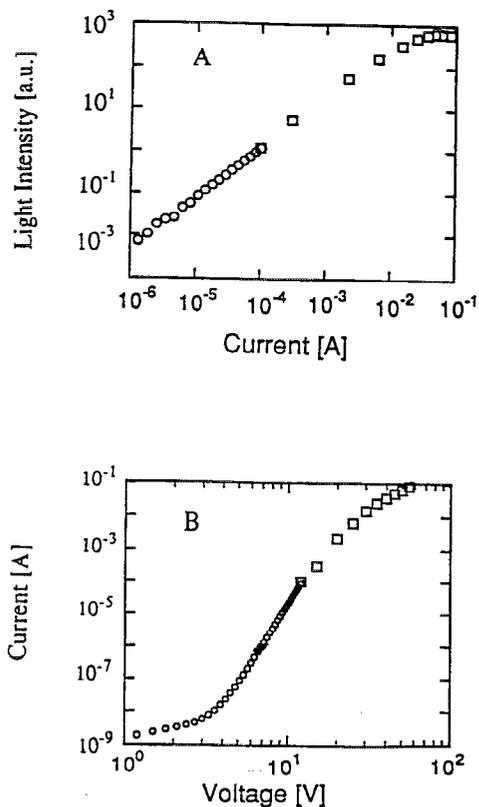


FIG. 3. Panel A plots light emission vs current, and panel B plots current vs voltage. Circles represent direct current response, and squares represent the response to a 0.5% duty-cycle square pulse with 200- μ s period.

material. Since the time constant for charging the capacitor is given by

$$1/\tau = 1/RC = (1/R_s C + 1/R_p C),$$

the decay time approaches $R_s C$ when R_p gets large; i.e., R_p can be increased to values sufficiently large that it is no longer of importance. In this way, one can expect to reduce the RC time to the point where measurements on the relevant time scales necessary to resolve and study the emission can be achieved.

To measure the EL intensity under low duty-cycle bias conditions, a 150-mm achromatic lens focuses the light into a single-grating monochromator (Spex 340S) with a Photometrics CCD camera (Tektronix TK512 CCD) as the detector. The integrated intensity provides the total light output. For dc measurements, the EL intensity is determined with a calibrated silicon photodiode. The device efficiency was approximately 0.1% (photons/electron) at a bias of 15 V and 4 μ A (the relatively low efficiency resulted from degradation during mounting of the device onto the transmission line and transferring the mounted device into the vacuum can).

Figure 3(a) shows the light intensity as a function of current flow, both for dc and 0.5% duty-cycle operation. The intensity is roughly linear over almost five orders of magnitude and saturates for currents above 40 mA corresponding to current densities above 10 A/cm². The current vs voltage characteristics for the same device appear in Fig.

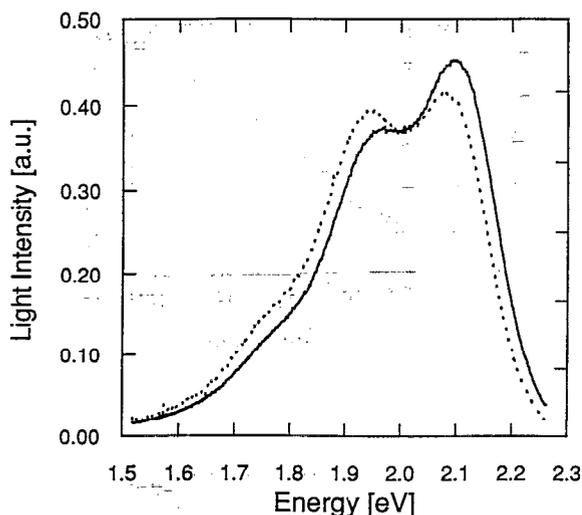


FIG. 4. Electroluminescence intensity vs photon energy for 0.5% duty-cycle pulses with amplitudes of 82.4 (solid) and 2.18 mA (broken). The low current spectrum has been scaled by a factor of 12.

3(b). Since polymer LED devices tested under direct current operation saturate, often catastrophically, at current densities in the range 20–100 mA/cm², the low duty-cycle pulsed operation enables emission levels more than two orders of magnitude above the dc level.

Recording the complete EL spectra during the high current density experiments has the advantage of allowing simultaneous monitoring of the details of the EL spectrum. At higher levels of current injection, the spectra change as shown in Fig. 4. For the sample whose data appear in Fig. 3, the EL spectra shift slightly to the blue as the EL intensity saturates. The spectra in Fig. 4 were recorded well into saturation at 0.218 mW average power and 22.7 mW average power, and they are shifted in energy by approximately 17 meV. At the onset of saturation, the device dissipates more than 1 W/cm² into the thin MEH-PPV film (thickness approximately 1200 Å). Since the thermal properties of the polymer film are poorly matched to the glass substrate and since no special attempt was made to heat sink the sample, significant heating is expected. Indeed, these semiconducting polymers are known to exhibit thermochromism with a spectral blue shift as the sample temperature is increased. The EL spectra also display such thermochromism.⁷ Since the observed blue-shift (Fig. 4) is

in the direction expected for sample heating, the saturation at the highest levels shown in Fig. 3 is probably due to heating. For other devices subjected to 0.1% and 0.05% duty-cycle pulses, no spectral shift was observed, and the saturation was correspondingly suppressed. Thus with proper heat-sinking and/or low duty-cycle pulses, it should be possible to extend the transient EL intensity to still higher values.

In conclusion, pulsed operation of light-emitting diodes made from a soluble semiconducting polymer provides additional information about the transient behavior of the electroluminescence and provides evidence that device saturation results from heating at high current densities. Device switching times observed in this work compare favorably with commercially available visible LEDs made from inorganic materials. Operation at higher current densities will require lower duty-cycles and/or improved heat sinking.

We thank F. Klavetter of UniAx Corporation for preparing the MEH-PPV and D. McBranch, G. Yu, and C. H. Lee for valuable discussions and assistance. This research was sponsored by the Electric Power Research Institute.

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