Improved Efficiency in Semiconducting Polymer Light-Emitting Diodes

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We report visible light emission from metal-polymer diodes made from semiconducting polymers, with indium-tin oxide as the "ohmic" contact, and a variety of metals as the barrier metal. Our results, which confirm the discovery by the Cambridge group [Nature *347*, 539 (1990)], demonstrate that light-emitting diodes can be fabricated by casting the polymer film on indium-tin oxide from solution with no subsequent polymer processing or heat treatment required. Electrical characterization reveals diode behavior with rectification ratios greater than 10^5 at sufficiently high voltages. Use of an electrode material with low work function leads to more than an order of magnitude improvement in the room-temperature efficiency of the devices. For example, the most efficient devices made with calcium as the rectifying contact display efficiencies of 0.01 photons per electron.

INTRODUCTION

The results of Burroughes et al.[1] show that semiconducting polymers serve as active light sources. Our work with other polymers and electrode materials demonstrates that electroluminescence from conjugated polymer diodes is a more general phenomenon. We report light emission from diodes fabricated with MEH-PPV, poly(2-methoxy,5-(2'-ethylhexoxy)-1,4-phenylene-vinylene).[2] MEH-PPV offers the advantage of being *soluble in the conjugated form* in organic solvents. The appropriate choice of electrode materials leads to significant improvement in luminescence efficiency. We describe device fabrication, simplified because of direct casting of the semiconducting polymer from solution, and we present the results of electrical and optical characterization.

EXPERIMENTAL

The light emitting diodes (LEDs) consist of a rectifying metal contact on the front surface of an MEH-PPV film on a glass or poly(ethylene terephthalate) substrate, partially coated with a layer of indium-tin oxide (ITO), the "ohmic" contact. Figure 1 displays the device geometry. The MEH-PPV films are prepared by spin-casting from tetrahydrofuran or xylenes solutions containing 1% MEH-PPV by weight. The resulting MEH-PPV films have uniform surfaces with thicknesses in the range of 500 to 2000Å. Metal contacts (barium, calcium, magnesium, or indium) are deposited on top of the poly-

mer films by vacuum evaporation at pressures below 10^{-6} Torr yielding active areas of 0.04 or 0.1 cm^2. All processing steps are carried out in a nitrogen atmosphere. Silver paint or indium solder provides contact between electrodes and external wires.

Spectroscopic measurements use a single-grating monochromator followed by a photodiode array or a photomultiplier tube with a lock-in amplifier as detector. Electroluminescence modulation is achieved by applying a sinusoidal voltage superposed on a DC voltage. The measurements are carried out with the LEDs in a nitrogen atmosphere or a vacuum cryostat at pressures below 10^{-4} Torr. Integrated intensity is determined with a calibrated silicon photodiode and corrected for the spectral response and the solid angle of the collecting optics.

Light from the LEDs appears yellow-orange, with thinner polymer films producing a slightly more yellow color. Figure 2 compares the room temperature electroluminescence spectrum of an LED made with an indium top electrode to that from a calcium device. The In/MEH-PPV diode produces light below the sensitivity of the photodiode array, so we employ the modulation technique with 3 V AC superposed (at 681 Hz) on 13 V forward bias. The luminescence peaks below 2.1 eV with a hint of a second peak at 1.9 eV. Because the Ca/MEH-PPV diode shines much brighter, the photodiode array can record the spectrum. Note that the brighter luminescence from the calcium device even resolves the third peak below 1.8 eV. The peaks agree quite well with those attributed to phonon emission in photoluminescence experiments with MEH-PPV.[3]

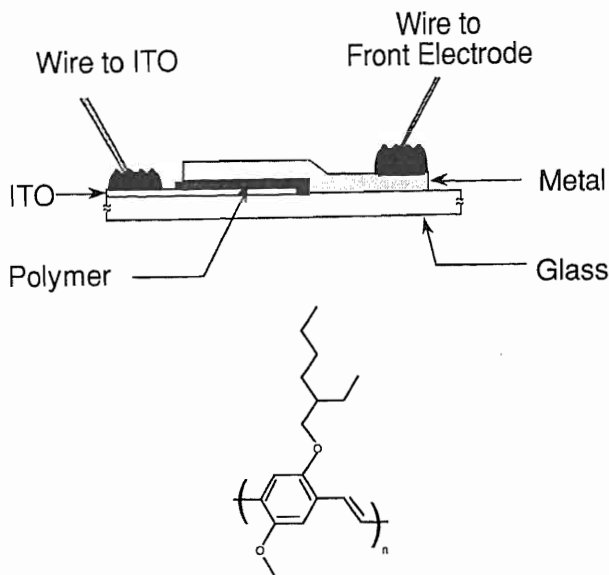Current vs voltage characteristics are shown for

Fig. 1 — Side view of device geometry. Under forward bias the light emerges from the bottom of the device. The inset shows the structure of MEH-PPV.

Fig. 3 — Current flow and light emission vs applied bias for light-emitting diodes with indium electrode (A) and calcium electrode (B). Solid curve is current. Symbols depict light emission.

a diode with indium top electrode in Fig. 3A. We define forward bias as a positive bias applied to the p-type polymer. While ramping the applied bias, yellow-orange light becomes visible to the eye just below 9 V forward bias (no light is observed under reversed bias). Above 15 V, the rectification ratio exceeds 10^4. The light is most easily observed in a dark room. The efficiency is as high as 5×10^{-4} photons per electron. The characteristics in Fig. 3B of a diode with calcium top electrode display the higher efficiency and lower turn-on voltage that result from using a lower work function electrode. The

light is clearly visible with room lights on for a bias above 4 volts, and the rectification ratio exceed 10^5. The efficiency improves to 0.01 photons per electron, a value comparable to those achieved in III-V visible light emitters such as GaP:N, and GaAs$_x$P$_{1-x}$:N.[4]

DISCUSSION

The band diagram of the rectifying junction postulated in Fig. 4 shows electron injection in forward bias, during light emission. Electron injection at the rectifying contact can lead to recombination in two ways: thermionic emission or tunneling. Thermal excitation of electrons from the metal would enable injection into the conduction band of the polymer (mechanism 1 in Fig. 4). After surmounting the barrier, self-localization will lead to the formation of a negative polaron, which recombines with a positive polaron to form the excited state of the neutral polaron exciton, a state with lower total energy than the two oppositely charged polarons because of the Coulomb attraction.[5,6] The excited state decays radiatively. Alternatively, electrons can *tunnel* from the rectifying contact through the barrier into the conduction band (2) or directly into the polaron gap states (3). All paths can lead to a radiative decay, but these mechanisms compete with the non-radia-
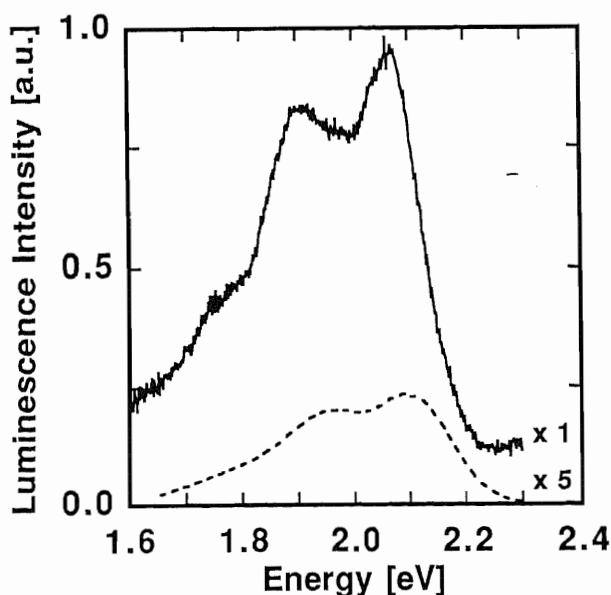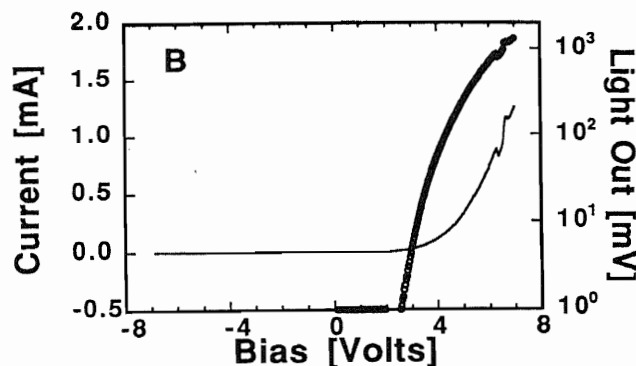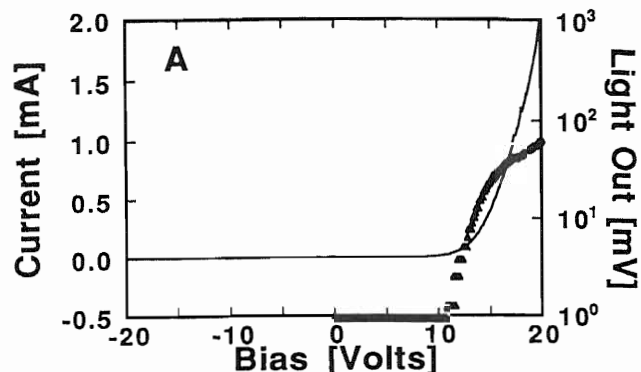

Fig. 2 — Electroluminescence intensity vs photon energy at room temperature. Solid curve is Ca/MEH-PPV diode under forward bias of 7.5 V dc bias. Dashed curve is In/MEH-PPV diode under a forward bias of 13 V dc with 3 V ac superposed at 681 Hz.
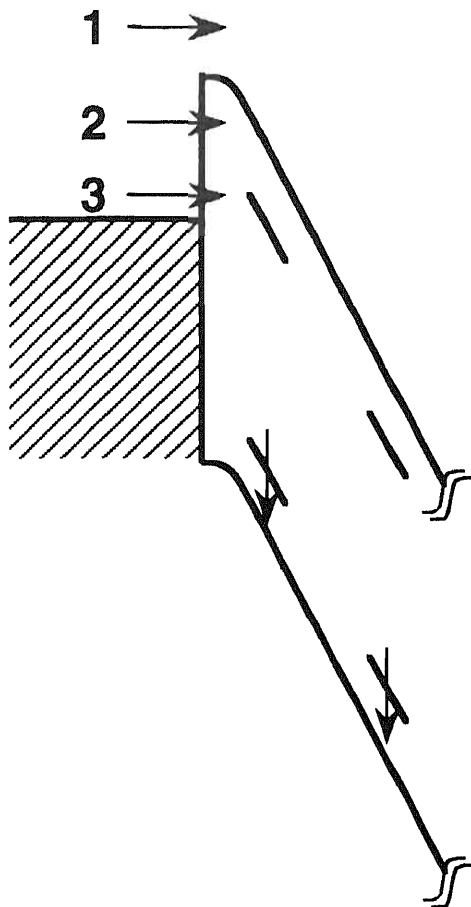
Fig. 4 — Energy band diagram of the rectifying junction in forward bias, suggesting electron injection routes: electrons can overcome the barrier thermally (1), or electrons can *tunnel* from the rectifying contact through the barrier into the conduction band (2) or directly into the polaron gap states (3).
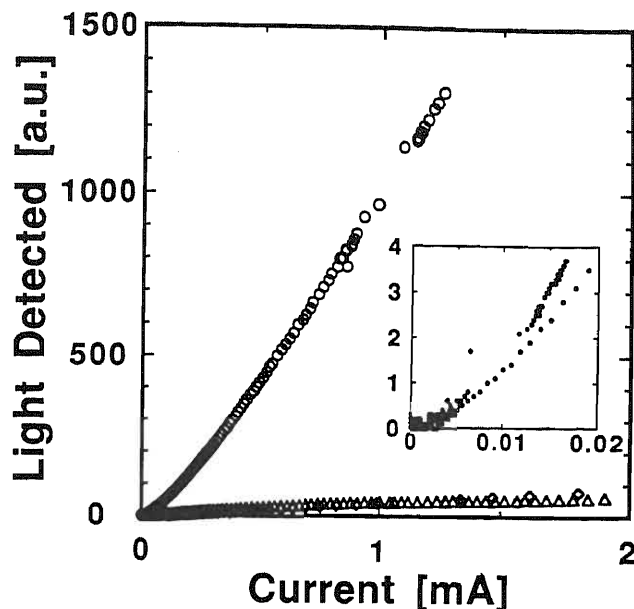

Fig. 5 — Light emission vs current for diodes with a variety of top electrodes: barium (dots), calcium (open circles), magnesium (squares), and indium (triangles). Inset shows barium and calcium devices.

tive injection of positive carriers from the polymer into the metal[7] and non-radiative recombination.[1]

Tunneling appears to be the more likely route for injection of carriers of both polarities. The current vs voltage characteristics change only slightly as a function of temperature, so majority carriers are not thermally driven. Independent evidence from the temperature-dependence of the current vs voltage characteristics also suggests that in diodes fabricated from semiconducting polymers carrier injection takes place via tunneling.[8] The band diagram of Fig. 4 also ignores the very likely formation of some type of interfacial layer at the junction with the rectifying metal. If this boundary creates a potential barrier, there would be an additional reason to suspect tunneling. At low temperature, the luminescence intensity increases, so electron injection has the opposite temperature dependence of a thermally driven process. The trends agree with the tunneling explanation and are incompatible with thermal activation.

This scheme suggests that increasing the barrier height for majority carriers and decreasing the barrier height for electrons at the rectifying metal contact would favor the light emission channel. The data

of Fig. 5 verify this prediction. Figure 5 displays the electroluminescence intensity as a function of current flow under increasing forward bias for LEDs made with four different metals as rectifying electrodes. The metals with lower work function, barium (2.7 eV) and calcium (2.87 eV) make more efficient LEDs than the metals with higher work functions, magnesium (3.66 eV) and indium (4.12 eV).[9] The electroluminescence intensity emitted by LEDs with calcium electrodes as the rectifying contact exceeds by more than an order of magnitude the EL intensity emitted by LEDs with indium electrodes. The external quantum efficiency at 1 mA is ≈0.05% for indium electrodes and ≈1.0% for calcium electrodes.

The modest electroluminescence efficiency results from the competition between the radiative processes and the non-radiative processes. Figure 6 displays the efficiency as a function of forward bias. The efficiency increase at higher bias suggests quenching of the non-radiative recombination possibly due to trap-filling.

CONCLUSION

The recent invention[1] of conducting polymer LEDs expands the possible applications for conducting polymers into the area of active light sources. Additional work with polymer preparation and electrode materials should provide further improvements in device efficiency. The structure of MEH-PPV shown in the inset to Fig. 1 reveals the desirable versatility that semiconducting polymers provide. Adjustments in the chemical structure allows bandgap engineering control of electronic and optical features while enabling independent control
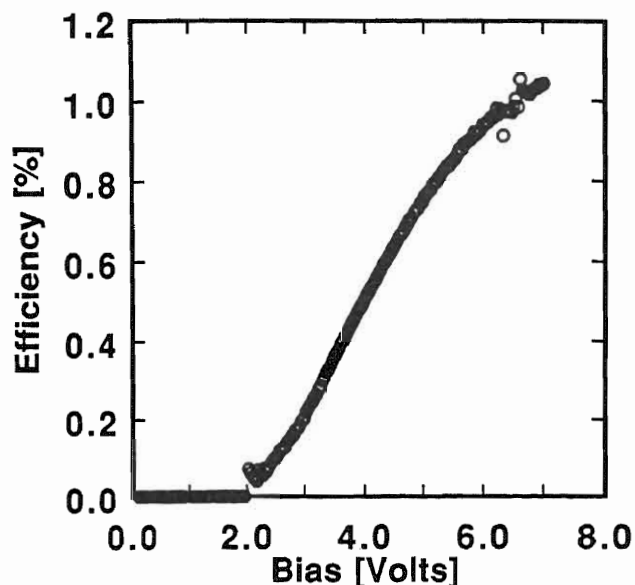
Fig. 6 — Electroluminescence efficiency [photons per electron] vs forward bias for Ca/MEH-PPV diode.

over chemical qualities. For example, the addition of alkoxy side groups to poly(1,4-phenylene-vinylene) reduces the energy gap and makes the semiconductor soluble. Controlling the energy gap of the polymer, either through the judicious choice of the conjugated backbone structure or through side-chain functionalization, should make possible a variety of colors.[10] Moreover, because of processing advantages of semiconductors cast from solution, large active areas can be envisioned. Thus, LEDs fabricated from conducting polymers offer a number of potential advantages to future technology.

ACKNOWLEDGMENTS

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