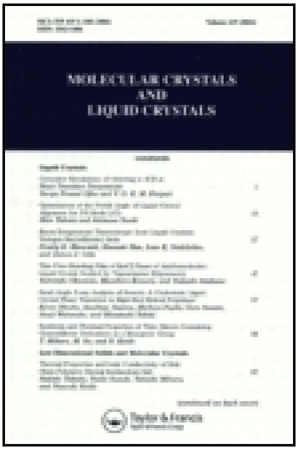

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MEH-PPV Light-Emitting Diodes: Mechanisms of Failure

J. C. Scott [a], J. H. Kaufman [a], J. Salem [a], J. A. Goitia [a], P. J. Brock [a] & R. Dipietro [a]

[a] IBM Research Division, IBM Almaden Research Center, 650 Harry Road, San Jose, CA, 95120-6099

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MEH-PPV LIGHT-EMITTING DIODES: MECHANISMS OF FAILURE

J.C. SCOTT, J.H. KAUFMAN, J. SALEM, J.A. GOITIA, P.J. BROCK AND R. DIPIETRO
IBM Research Division, IBM Almaden Research Center, 650 Harry Road, San Jose CA 95120-6099

Abstract Organic light-emitting diodes show increasing promise for technological application. Polymer based systems, although offering some processing advantages over LEDs based on organic small molecules, have not yet demonstrated sufficient stability for commercial devices. We have therefore undertaken a study aimed at identifying the degradation mechanisms in LEDs fabricated from a single layer of MEH-PPV between ITO as transparent anode and calcium as cathode. Current-voltage, luminance, spectroscopy and in-situ IR measurements were made. The results reveal several processes leading to reduced power conversion efficiency and eventual failure. Chemical degradation of the polymer, even in devices protected from ambient oxygen, both reduces its ability to transport charge and introduces carbonyl moities which quench the luminescence. FTIR spectroscopy provides details of the chemical processes involved and indicates that ITO can act as an oxygen reservoir in the formation of aromatic aldehydes. Additionally, inhomogeneous degradation occurs by the formation of "hot-spots" which shunt current from the remainder of the device area. Such areas may eventually become electrically open, perhaps due to thermal runaway, thereby reducing the active area of the diode.

INTRODUCTION

The observation of electroluminescence in poly(phenylenevinylene) (PPV) by Burroughes et al. in 1990[1] has sparked a high degree of interest because of the obvious potential in flat-panel display technology. The low operating voltage, high brightness, thinness, light weight, Lambertian emission and flexibility are all appealing features. The properties which require additional improvement for viable technology include luminous efficiency, color gamut and operating lifetime the last of which presents the greatest challenge.[2] We have undertaken a study of the degradation and failure of polymer LEDs. Specifically, we report data from single layer devices based on poly(2-methoxy-5(2'-ethyl)hexoxy-1,4-phenylenevinylene)[3] (MEH-PPV). These can last up to a few hundred hours when operated in a dry, inert atmosphere. Our approach is to monitor the electrical (current-voltage, capacitance-voltage, and ac impedance), optical (luminance *vs.* current, spectrum) and chemical characteristics (***in-situ*** FTIR) of a device as it ages. We then examine failed devices by Auger depth profiling, and by scanning electron microscopy (SEM). This paper is a summary of our results, further details of which are reported elsewhere.[4]

EXPERIMENTAL

MEH-PPV was synthesized using slight modifications of literature procedures.[5] LEDs, of area 0.1 cm^2, were fabricated on glass substrates with the structure illustrated in Figure 1. The polymer layer, 700 Å thick, was spin-coated from *p*-xylene solution inside a glove-box containing dry nitrogen. FTIR spectra were taken in reflection mode on three types of sample: MEH-PPV spin coated onto a gold mirror on a Si wafer; spin-coated on an ITO layer on a gold mirror; and in a diode structure with ITO anode and Ca cathode, again on Si. All electrical, optical and FTIR measurements were made either with the samples inside the glove-box or in hermetic holders fitted with electrical feedthroughs and quartz windows. For Auger analysis and electron microscopy, the samples were exposed briefly to the atmosphere.

RESULTS

Figure 1 shows characteristic aging behavior of a diode illustrative of all those tested to date. The voltage rises steadily starting from the very beginning of the run, indicating an increase in the dc impedance of the device. At the same time the luminous output drops, i.e., the quantum efficiency, decreases. The phase of gradual degradation is frequently interrupted by a sudden drop in voltage and, as in the LED of Figure 1, by complete loss of light output. The voltage-drop signals the appearance of a short in the device. Most such shorts do not last very long, because the cathode cannot support the high local current density. The short reopens and the voltage rises again, driving current though a wider area of the diode. In many cases, the diode again emits light, now at lower total intensity and in the last stages quite inhomogeneously.

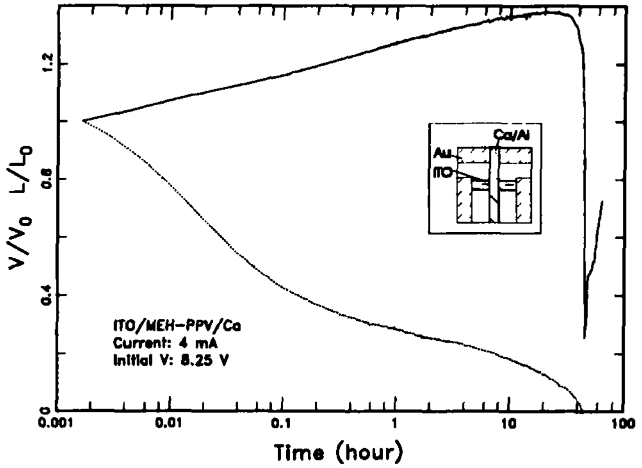

Figure 1. LED aging at constant current in a nitrogen showing the voltage (solid line) and luminance (dotted) each relative to their initial values. Note the semi-logarithmic scale. The inset shows the geometry of the diode.

The zero-bias capacitance changes by little as 1% until the last few hours before complete burn-out when it drops rapidly by 50% or more. This is due to loss of active area caused by burn-out of shorts, and is consistent with SEM imaging which shows areas of about 10 microns diameter where the metal of the cathode has melted and receded from the center of the short.

From various model compounds and tables[6] we have identified several IR modes of MEH-PPV. (Our assignments differ significantly from those of Voss[7] *et al.*) Those relevant to the degradation chemistry include the three "semi-circular stretch" modes of the phenyl ring at 1415, 1506, and especially 1608 cm^{-1} which is not IR active on a symmetric ring and only very weakly active in MEH-PPV. There are two modes associated with C-O bonds, at 1208 arises from the phenyl-oxygen stretch, and at 1044 due to the O-alkyl modes. The vibration at 969 cm^{-1} arises from the olefinic trans-CH wag and is a signature of the conjugation of the polymer.

The degradation of the polymer due to UV exposure on ITO is revealed in changes in the IR spectrum at 1100-1200 cm^{-1}, the absorption of the ITO layer itself, and indicates a reduction in its partial oxidation state. Exposure of samples spun on gold, as well as on ITO, exhibit new carbonyl signatures due to aromatic aldehyde. Thus ITO cannot be the only source of carbonyl oxygen. In both cases the vinylene trans-CH wag was also seen to decrease in intensity implying a loss of conjugation.

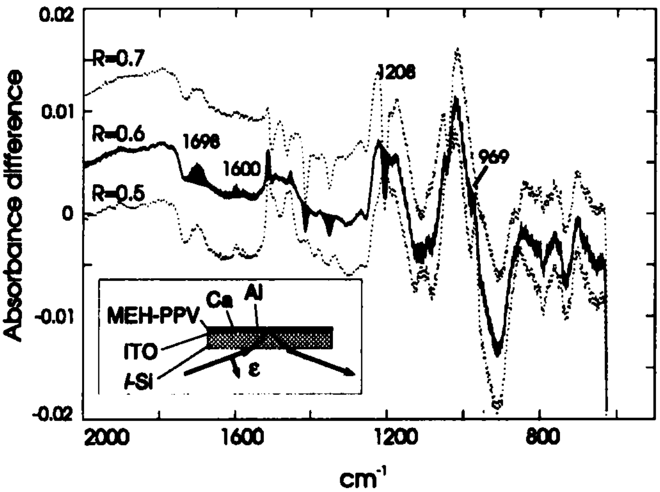

Figure 2. IR difference spectrum of MEH-PPV run in a functional diode. The curves are labeled by the number ***R*** in $A_{after}-RA_{before}$, where ***A*** is the measured absorbance. ***R*** is adjusted to minimize the parent peaks of the original spectrum. A large peak at 1200 cm^{-1} has been digitally subtracted from the data. The inset shows the structure of the diode used to obtain the spectrum.

FTIR also reveals chemical changes in a functional diode. Figure 2 shows the difference in IR absorption when 8000 C/cm^2 passed through a device. Since not all the polymer reacts (degrades), the reference spectrum of the pristine diode must be normalize by a factor, ***R***, which gives the fraction of unmodified polymer remaining at the end of the experiment. The most dramatic difference in the IR data is the change in absorption around 1100-1200 cm^{-1} which arise from the partially oxidized ITO anode. This feature has been numerically removed from the data of Figure 2 in order to reveal more clearly the changes in MEH-PPV. As in the UV treated samples, aromatic aldehyde formation is observed with the CO mode (1698 cm^{-1}) somewhat higher than before, indicating reduced conjugation of the phenylene units. We also observe a decrease in the olefinic trans-CH wag at 969 cm^{-1}, and a loss in the 1208 cm^{-1} phenyl-oxygen stretch.

Increased absorption at 1608 cm^{-1} indicates a breaking of ring symmetry as expected with formation of aromatic aldehyde.

DISCUSSION AND CONCLUSIONS

The experimental data presented in the previous section can be interpreted in terms of two distinct failure mechanisms. First, oxidation of MEH-PPV to aromatic aldehydes leads to a loss in luminous efficiency due to quenching by carbonyl. At the same time, the polymer becomes a poorer charge transport medium and the device impedance increases. These conclusions are supported by the luminance, IV and FTIR measurements. The oxidation process starts at the very beginning of diode life and proceeds steadily as they are run. The second mechanism leading to eventual failure is the formation of shorts which "repair" themselves by fusing the cathode material in an area around each site. This reduces the active area of the device. The evidence for this mechanism comes from the constant-current aging behavior of voltage and luminance, from IV characteristics, and from current-luminance data. The loss in active area is seen as a reduction in capacitance especially towards the end of life. Optical images show inhomogeneous emission, and the aftermath of the shorting process is clearly revealed by SEM and Auger elemental analysis.

Photo-oxidation of PPV polymers has been thoroughly characterized,[8] and is well known to lead to the formation of carbonyl quenching centers. Analysis of the spectra presented in this work reveals that the carbonyl is present as aromatic aldehyde, and moreover that polymer conjugation is reduced, resulting in lower mobility. These observations suggest that the oxidation occurs by a mechanism similar to that of olefin ozonolysis.[9] The dominant source of oxygen is ITO itself, a non-stoichometric oxide, meta-stable over a range of oxygen concentration. The FTIR spectra reveal significant loss in the oxygen vibrational mode and strongly suggest that ITO acts as an oxygen reservoir. The reduction of conjugation does not cause a significant spectral change in the emitted light. One might expect a blue shift as the conjugation length is reduced, but since the breaks in conjugation are accompanied by the formation of quenching centers, excitons on the broken polymer chains are most readily quenched and contribute little to the emission.

The evidence available to date does not allow the identification of the origin of the shorts which form in the last stages of diode life. We suggest, however, that once the initial "hot-spot" has formed, thermal runaway leads to catastrophic local failure. Both charge injection and mobility increase with temperature. Thus any small area with above average current heats more and further lowers its impedance. When the fused areas start to merge significantly the electrical continuity of the cathode is broken. Final failure of the diode is then quite rapid.

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