

Influence of Intensive Light Exposure on the Complex Impedance of Polymer Light-Emitting Diodes

Fábio Rogério Cury^{a}, Thiago Cazati^b, Rodrigo Fernando Bianchi^a*

^a*Departamento de Física, Campus Morro do Cruzeiro, Universidade Federal de Ouro Preto
35400-000 Ouro Preto - MG, Brazil*

^b*Instituto de Física de São Carlos, Universidade de São Paulo
Avenida Trabalhador São Carlense, 400, 13560-970 São Carlos - SP, Brazil*

Received: December 5, 2007; Revised: June 3, 2008

In this work we investigated the effect of visible radiation on the electrical properties of poly[(2-methoxy-5-hexyloxy)-p-phenylenevinylene]-MH-PPV films and light emitting diodes. Complex impedance measurements of (Au or ITO)/MH-PPV/(Au or Al) samples were carried out at room temperature and exposed to white light. Over the frequency range from 100 mHz to 2 MHz, the electrical results of Au/MH-PPV/Au was dominated by the Cole-Cole approach, where the electrode influence is negligible. However, some additional influence of the interface was observed to occur when Al was used as electrode. These effects were observed under both dark and visible-light illumination conditions. A simple model based on resistor-capacitor parallel circuits was developed to represent the complex impedance of the samples, thereby separating bulk and interface contributions. We observed that the polymer electrical resistivity decreased while the dielectric constant of the polymer and the thickness of the Al/MH-PPV layer were almost constant with increasing light intensity. The decrease of the polymer layer resistance comes from a better charge injection due to a light induced dissociation of positive charge carriers at the electrode.

Keywords: *polymer, device, photoconductivity, interface*

1. Introduction

Since the first report of polymer light-emitting diodes (PLED) in 1990¹, there has been a considerable effort to improve the efficiency and understanding the electrical properties of such devices. However, many aspects related to the carrier transport mechanisms remain unclear or is somewhat controversial^{2,3}. For example, although the carrier transport mechanism through the electroluminescent polymers is usually described as a stochastic process between hopping sites, the carrier injection from the electrode into the polymer is frequently attributed to tunneling of electrons and holes in polymer rigid bands. From this point of view, the ac conductivity appears as a powerful technique able to investigate the electrical properties of PLEDs, since it can be used to study not only the carrier transport mechanism⁴ through the polymer bulk, but also to investigate the influence of the polymer-electrode interfacial layer⁵, as well as the influence of humidity, light exposure, temperature etc. in the optical and/or electrical characteristics of such devices⁶. In this context, the goal of this paper is to progress in the elucidation of the effect of light-induced conductivity variation of polymer light-emitting diodes when exposed to visible radiation.

2. Experimental Procedure

Poly[(2-methoxy-5-hexyloxy)-p-phenylenevinylene]-MH-PPV was chemically synthesized using a method described elsewhere⁷. MH-PPV solution (6% (wt)) in chloroform was spincoating on glass recovered with a thin indium-tin oxide (ITO) films and on a gold layer, previously deposited on glass/chromium substrates. Gold and aluminum metallic cathodes were thermally evaporated on the polymer layer, where the electrode area (A) is around $3 \times 10^{-5} \text{ m}^2$ and polymer thickness (L) around 400 nm obtained by atomic force microscopy (AFM). Figure 1 shows the polymer film and light-emitting diodes structures configurations. Current density vs. voltage (J vs. V) curves

were carried out in a Keithley 237 Unit, while complex impedance measurements, $z^*(f) = z'(f) - iz''(f)$, on the other hand, were carried out in a 1260 Solartron Frequency Response Analyzer in the 100 mHz to 2 MHz frequency range, oscillation amplitude equal to 50 mV. The incident light was provided by a 250 W tungsten lamp served as a source of white dichroic light, which has focused onto the entrance window of the cryostat. Different intensities of light (0.60 or 250 mW.cm²) illuminated the sample in order to investigate the effects of illumination on their electrical behavior. To prevent photo-oxidation, the samples were placed in a vacuum cryostat at pressure $\sim 10^{-5}$ Torr. All measurements were performed at room temperature (300 K) in a dark room and only conducted after the samples were illuminated up to 5 minutes.

3. Experimental Results

Figure 2 shows the current density vs. voltage (J vs. V) curves of ITO/MH-PPV/Al structure presented in Figure 1. The measurements were carried out in under different illumination conditions (dark, 60 mW.cm⁻² and 250 mW.cm⁻²). From these results, the typical Schottky diodes behavior is observed, in which the threshold voltage (V₀) is around 1.0 V for all intensities. After threshold, the current density of ITO/MH-PPV/Al device is directly proportional to light intensity suggesting that the dc electrical resistivity of the polymer film (obtained from Ohm's Law for $V > V_0$) decreases with increasing the intensity. It means that this polymer shows photo-conductivity behavior. Furthermore, non-linear current-voltage dependence has been observed in poly(p-phenylenevinylene) derivatives light-emitting diodes when ITO-Al were used as electrodes⁴, which contrast with the linear dependence (or ohmic behavior), observed when ITO-Au or Au-Au were used as electrodes^{8,9}. This linear dependence is explained in terms of ohmic contact obtained from the ionization

*e-mail: cury@aluno.demin.ufop.br

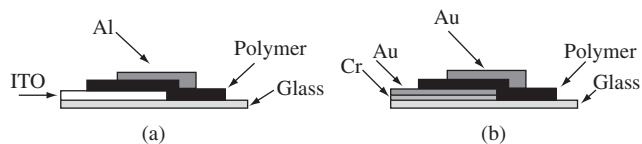


Figure 1. Schematic representations of the polymer structures used in this work. a) ITO/MH-PPV/Al and b) Au/MH-PPV/Au.

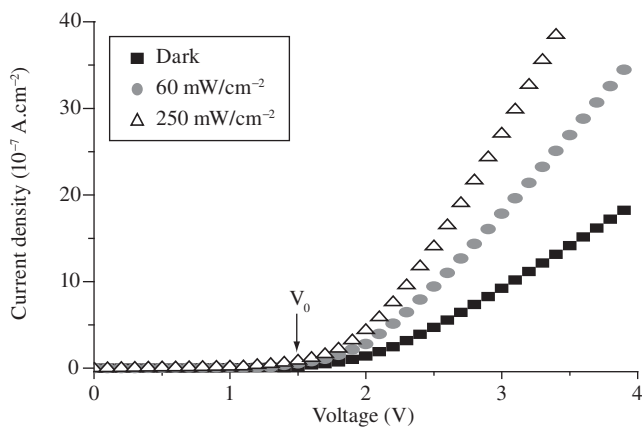


Figure 2. Current density vs. voltage (J vs. V) curves of ITO/MH-PPV/Al structure performed in vacuum and under different illumination conditions (dark, 60 mW.cm^{-2} and 250 mW.cm^{-2}).

potential of MH-PPV (5.2 eV) and work functions of the Au or ITO (around 5.1 eV).

Figure 3 shows the frequency dependence of the real, $Z'(f)$, and imaginary, $Z''(f)$, components of the complex impedance of both Au/MH-PPV/Au and ITO/MH-PPV/Al samples. The measurements were carried out in the dark for Au-Au (Figure 3a), and in the dark (Figure 3b), and at 60 mW.cm^{-2} (Figure 3c) and at 250 mW.cm^{-2} (Figure 3d) for ITO-Al. At low frequencies we have observed that real component of Au-Au (Figure 3a) exhibits a plateau, at about $8 \text{ M}\Omega$ that extends up close to 100 Hz. Beyond this frequency, denominated here as the critical frequency f_c , $Z'(f)$ decreased continuously, and at 1 MHz the recorded value of around $50 \text{ }\Omega$. On the other hand, the imaginary part has showed a broad peak with the maximum around f_c . This is the typical behavior of disordered materials being $\sigma_{dc} = L/AZ_0 = 1.5 \times 10^{-8} \text{ S/m}$ the dc conductivity of the polymer. For frequencies higher than 10 Hz, $Z'(f)$ and $Z''(f)$ of ITO-Al sample presented a similar Au-Au behavior. However, the f_c increased while the $Z'(f_c)$ decreased with increasing light intensity. Moreover, $Z'(f)$ and $Z''(f)$ increased when $f \rightarrow 0$, and $Z''(f)$ presented a minimum at about 10 Hz in dark condition which shift towards higher frequencies with illumination. These results suggest that the interface Al/MH-PPV dominates the real and imaginary components of the impedance at lower frequencies (below f_c), while the polymer film dominates at higher frequencies (above f_c). Full lines in Figure 3 represent the theoretical-experimental fittings obtained from Equation 2, as discussed in section 4.

4. A Model for Complex Impedance

The clear distinction between bulk and interface effects on the complex impedance suggested through the results showed in Figure 3 makes it possible to assume the total impedance (Z^*) of ITO/MH-

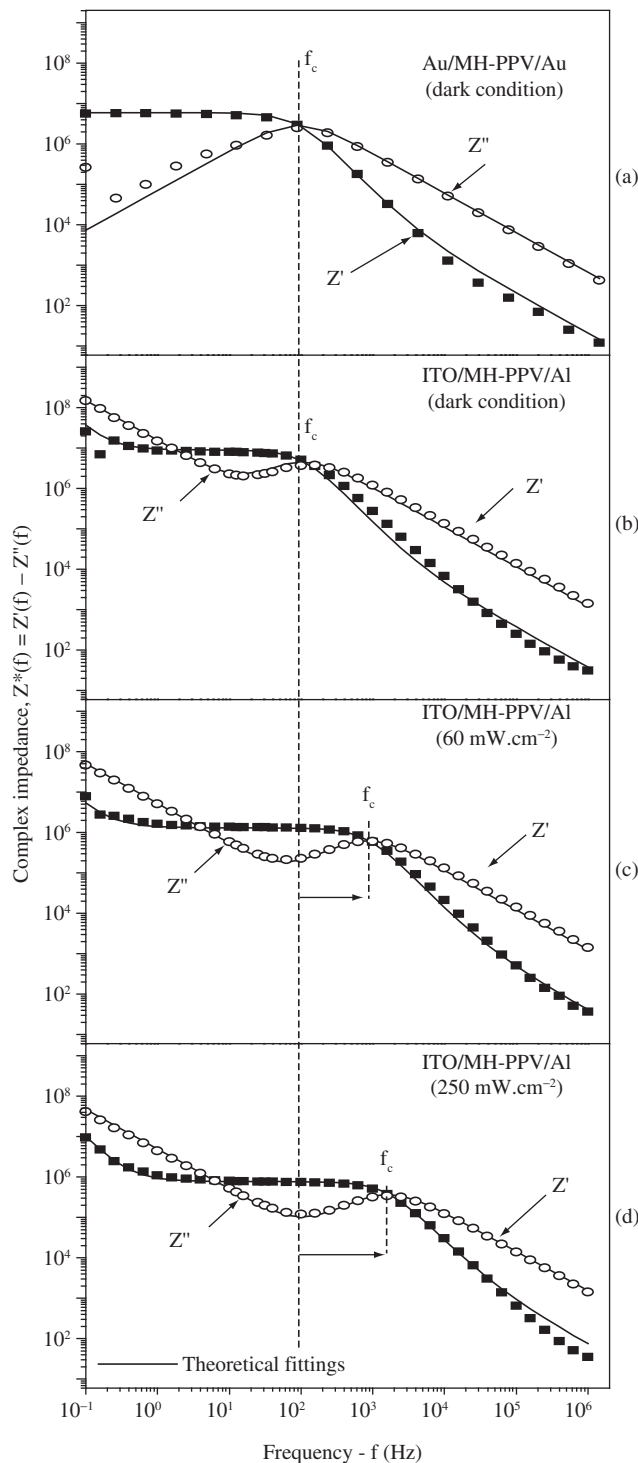


Figure 3. Real, $Z'(f)$, and imaginary, $Z''(f)$, components of the complex impedance for Au/MH-PPV/Au and ITO/MH-PPV/Al samples. The measurements were carried out in the dark for Au-Au (Figure 3a) sample, and in the dark (Figure 3b), at 60 mW.cm^{-2} (Figure 3c) and at 250 mW.cm^{-2} (Figure 3d) for ITO-Al one.

PPV/Al diodes as an expression based on the series combination of bulk impedance of MH-PPV film (Z_p^*), the impedance of Al/MH-PPV interface layer (Z_i^*) and the resistance of ITO (Z_{ITO}^*), such that:

$$Z^* = Z_i^* + Z_p^* + Z_{ITO}^* \tag{1}$$

We further assume Z_p^* , Z_i^* and Z_{ITO}^* to represent a combination of a resistor in parallel with a capacitor obeying the Cole-Cole expression¹⁰, and Equation 1 becomes:

$$z^*(f) = \frac{R_i}{1 + (i2\pi/R_i C_i)^{\alpha_i}} + \frac{R_p}{1 + (i2\pi/R_p C_p)^{\alpha_p}} + R_{ITO} \quad (2)$$

where f is the electrical-field frequency and the parameters α_i and α_p simulate distributions of relaxation times of the MH-PPV and Al/MH-PPV, such that $0 \leq \alpha_p, \alpha_i \leq 1$. Of course, when $\alpha_i = \alpha_p = 0$, we have the classical Debye process¹⁰ (or single time constant).

5. Discussion

The full-line curves in Figure 3 show the fitting of the experimental results obtained using Equation 2 for samples with Au-Au and ITO-Al electrodes in the dark, as well as for ITO/MH-PPV/Al sample also under illumination, with the adjusted parameters values given in Table 1. It is observed that R_p for ITO-Al sample varied from 6 M Ω (dark) to $7.7 \times 10^5 \Omega$ (under higher illumination conditions), and therefore its polymer film parameters obtained in the dark are similar to those obtained for Au-Au sample at the same condition. This result suggests that the impedance of the MH-PPV film on ITO/MH-PPV/Al device decreases with the light intensity, as expected from the analysis of Figure 2, in which the tangent dJ/dV increased with increasing light intensity. In addition, the capacitance and resistance of the interface is higher than the values obtained from the polymer, and almost all parameters decreased with increasing light intensity. These results suggest that the illumination acts increasing C_i and decreasing R_p , C_p , R_i , and thus the electrical resistivity of both polymer and interfacial layer ($\rho \approx AR/L_s$) and dielectric constant ($k_p \approx C_p L/\epsilon_0 A$) of the polymer, as well as the electrical resistance and the thickness of the Al/MH-PPV interfacial layer ($L_i \approx \epsilon_0 A/C_p$). Assuming that the electrical conductivity of material is directly proportional to the charge carrier mobility (μ) and to the density of charge carriers (n), ($\sigma \propto \mu n$), that σ/γ_{min} is proportional to $(1/R)/(1/\tau)$, where, σ is the conductivity, τ the relaxation time ($\tau = RC$), R the resistance and C the capacitance, ($C = Q/V$), where Q it is the amount of charge that can be storage at a capacitor with a capacitance C and a voltage V . One can say that σ/γ_{min} is proportional to C so the higher the conductivity is the higher the capacitance will be. If C_i increases it leads to an increase of the amount of charge storage hence the voltage is constant. It leads to an increase of the density of charge carriers, confirmed by the decreases of the electrical resistivity, as well-known for photo-conductive material, in which the density of photo-generated charges carriers is directly proportional to light intensity.

6. Conclusions

In this work we showed the influence of intensive light exposure on the real and imaginary components of the complex impedance of polymer light-emitting diodes. It was observed that the electrical

behavior of this device is controlled not only by the bulk properties of thin MH-PPV films, but also by the Al/MH-PPV interfacial layer. In order to obtain an expression to explain the experimental results, it was used a combination of resistor-capacitor circuits thereby separating bulk from interface contributions. Following the hint suggested by the parameters showed in Table 1, the dark conductivity and dielectrics constant of the polymer film, around 10^{-8} S/m and 3, are in agreement with literature^{8,9}, and thus a rough estimation for the thickness of the Al/MH-PPV layer may be obtained as few nanometers. Furthermore, the incident light provides photo-generated charge carriers at the bulk level increasing the conductivity, evidencing the photo-conductivity of material.

Acknowledgments

This work was sponsored by FAPEMIG, Fapesp and CNPq and IMMP/CNPq.

References

- Burroughes JH., Bradley DDC., Brown AR., Marks RN., Mackay K., Friend RH., Burns PL., Holmes AB. Light-emitting diodes based on conjugated polymers. *Nature* 1990; 347(6293):539-541.
- Arkhipov VI., Emelianova EV., Tak YH., Bässler H. Charge carrier transport and recombination at the interface between disordered organic dielectrics. *Journal of Applied Physics* 1998; 84(2):848-856.
- Davids PS., Campbell IH., Smith DL. Device model for single carrier organic diodes. *Journal of Applied Physics* 1997; 82(12):6319-6315.
- Brütting W., Berleb S., Mückl AG. Device physics of organic light-emitting diodes based on molecular materials. *Organic Electronics* 2001; 2(1):1-36.
- Bianchi RF., Cunha HN., Faria RM., Leal Ferreira GF., Mariz G., Neto J. Electrical studies on the doping dependence and electrode effect of metal-PANI-metal structures. *Journal of Physics D: Applied Physics* 2005; 38(9):1437-1443.
- Santos LF., Bianchi RF., Faria RM., Mergulhão S. Photogenerated carrier profile determination in polymeric light-emitting diodes by steady-state and transient photocurrent measurements. *Materials Science Engineering: B* 2006; 135(2):103-107.
- Bianchi RF., Balogh DT., Tinani M., Faria R., Irene EA. Ellipsometry study of the photo-oxidation of poly[(2-methoxy-5-hexyloxy)-p-phenylenevinylene]. *Journal of Polymer Science Part B: Polymer Physics* 2004; 42(6):1033-1041.
- Santos LF., Bianchi RF., Faria RM. Electrical properties of polymeric light-emitting diodes. *Journal of Non-Crystalline Solids* 2004; 338-340:590-594.
- Bianchi RF., Santos LF., Faria RM. *Complex Resistivity of polymer light emitting diodes*. In 11th International Symposium on Electrets- ISE 11; 2002. Melbourne: International Symposium on Electrets Proceedings; 2002, v.11. p. 359-362.
- Böttcher C.J.F., Bordewijk P. *Theory of electric polarization*. 1st ed. Local: Elsevier Scientific Publishing Company; 1978. v.II. p.62.

Table 1. Data of fittings between Equation 2 and experimental results for Au/MH-PPV and ITO/MH-PPV/Al exposed to different light intensities. For all fitting it was obtained $\alpha_p = \alpha_i = 0.98$ and $R_{ITO} \sim 30 \Omega$.

Sample	Light intensity (mW.cm ⁻²)	R_p (Ω)	R_i (Ω)	C_p (F)	C_i (F)	ρ_p (Ω cm)	L_i (m)	τ_p (Hz ⁻¹)	τ_i (Hz ⁻¹)
Au/MH-PPV/Au	Dark	6.0×10^6	-	1.8×10^{-9}	-	4.5×10^{10}	-	1.1×10^{-2}	-
ITO/MH-PPV/Al	Dark	9.0×10^6	9.0×10^8	1.0×10^{-9}	6.6×10^{-8}	6.7×10^{10}	4×10^{-9}	9.0×10^{-3}	59.4
ITO/MH-PPV/Al	60	1.3×10^6	8.0×10^8	9.0×10^{-10}	2.0×10^{-7}	9.8×10^9	1.3×10^{-9}	1.2×10^{-3}	160
ITO/MH-PPV/Al	250	7.7×10^5	2.6×10^8	7.9×10^{-10}	2.1×10^{-7}	5.6×10^9	1.2×10^{-9}	6.1×10^{-4}	54.6