# Charge Carrier Injection and Transport in PPV Light Emitting Devices

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**Abstract**
Charge carrier injection and transport in light emitting devices based on poly-phenylene-vinylene are investigated by internal photoemission and thermally stimulated currents. The barrier heights for electron injection depend very weakly on the metal work function, indicating a significant influence of surface states or interfacial layers. Trap states in PPV are detected with trap energies ranging from 0.1eV in fresh samples to 0.9eV in aged samples.
*Keywords: Poly(phenylene vinylene), Metal-semiconductor interfaces, Schottky barrier*

## 1. Introduction

Poly-phenylene-vinylene (PPV) was the first conjugated polymer where electroluminescence (EL) was observed.[1] Due to its good processability and high stability PPV and its derivatives are still attractive candidates as active materials for future organic electroluminescent display applications.

Monolayer light emitting devices (LEDs) from PPV usually show relatively low luminous efficiencies. These low values are a consequence of the fact that in PPV there is a strong imbalance of current flow for electrons and holes. It has been shown in measurements of current-voltage and capacitance-voltage characteristics that the p-type organic semiconductor PPV forms a Schottky contact with low work function metals like Ca or Al.[2] Electroluminescence in these devices is observed in forward bias direction at voltages exceeding values as low as 2V. However, since Schottky diodes are majority carrier devices, there is a large excess hole current, which does not recombine with the electrons injected at the metal electrode. Additionally, as a consequence of the inequality of the mobilities of electrons and holes, the recombination takes place near the polymer-metal contact, which possesses a large number of non-radiative pathways.

Beside the usage of metal-insulator-semiconductor (MIS) device structures[3] we have achieved an increase of external quantum efficiencies by using oxadiazole polymers[4] and small molecules[5] as an electron injecting/hole blocking layer between PPV and the metal electrode. External quantum efficiencies of 0.1% at a brightness of several hundred cd/m$^2$ have been achieved under driving conditions of about 100mA/cm$^2$ at 15V.

Apart from the luminescence properties of the active material, an understanding of charge carrier injection and transport is necessary for further improvements of these devices. In the following we will present investigations on the barrier for charge carrier injection by internal photoemission and on charge carrier traps by thermally stimulated currents.

## 2. Internal Photoemission

From a simple energy diagram of ITO/PPV/metal devices (Fig. 1) it is seen that there is only a small barrier of about 0.3eV for the injection of holes into PPV. This value may be even lower, because there occurs a doping of PPV during the elimination process on ITO by an In-Cl compound.[2] Thus the limiting factor of these devices is the barrier for electron injection at the metal/PPV interface. Given the electron affinity $\chi$ of the polymer (about 2.7eV for PPV) the barrier height for electrons follows directly from the metal work function: $\Phi_{B,e} = \Phi_M - \chi$. However it is most likely that depending on the preparation conditions the barrier heights are modified by the presence of interfacial layers and surface states. This has been already observed in metal/inorganic semiconductor interfaces, where the Schottky barriers in general do not follow the electron affinity rule.[6]

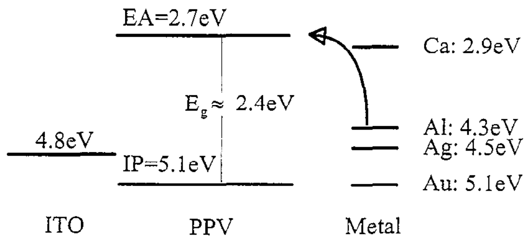


*Fig. 1: Energy diagram of ITO/PPV/metal devices*

Therefore the barriers for the injection of electrons from metal electrodes into the polymer PPV have been determined directly by internal photoemission (IPE). IPE is measured by detection of the photocurrent response to an incident light beam of variable photon energy.[6] Fig. 2 shows the IPE spectrum of an ITO/PPV/Al device, where the illumination was through the ITO. At wavelenghts of about 480nm there is a peak detected which is due to the generation of free carriers inside the polymer, this is the usual photovoltaic effect described before.[7] Additionally, there is a second signal shown in the inset of Fig. 2, which peaks at about 850nm. According to the theory of Fowler,[6] the photoresponse should follow a quadratic dependence on the incident photon energy: $R \propto (E-\Phi_B)^2$ with the barrier energy $\Phi_B$. Therefore we have plotted the square root of the signal as a function of the photon energy in the lower graph of Fig. 2. From a linear extrapolation to the energy axis a barrier height of about 0.7eV can be determined for Al. From the quantitative description of current-voltage characteristics with the Shockley equation we have determined the barrier for holes at the Schottky contact as $\Phi_{B,h}$=1.4eV.[2] Therefore, we ascribe this process seen in IPE to the injection of electrons from the Fermi energy of the metal to the conduction band of PPV. This assumption seems reasonable, because the sum of the hole and electron barrier (2.1eV) approximately satisfies the condition $\Phi_{B,h}+\Phi_{B,e}=E_g$. For further proof we have investigated IPE on devices with different metal electrodes, including Ca, Al, Ag and Au. Fig. 3 shows the resultant barrier heights as a function of the metal work function. It is seen that the barrier height follows a linear dependence on the work function of the form: $\Phi_{B,e} = 0.1\ \Phi_M + 0.36\text{eV}$. For comparison in Fig. 3 are also given the two limiting cases of the electron affinity rule and the case of a barrier totally pinned by surface states. The weak dependence of the barrier height on the metal work function (expressed by the small slope of 0.1) shows that there is a significant influence of surface states or interfacial layers in the injection process of carriers from metals into PPV. This is comparable to the results obtained by another group on devices with alkoxy substituted PPV, where a dependence of the form $\Phi_{B,e} = 0.26\ \Phi_M - 0.15\text{eV}$ has been found.[8]

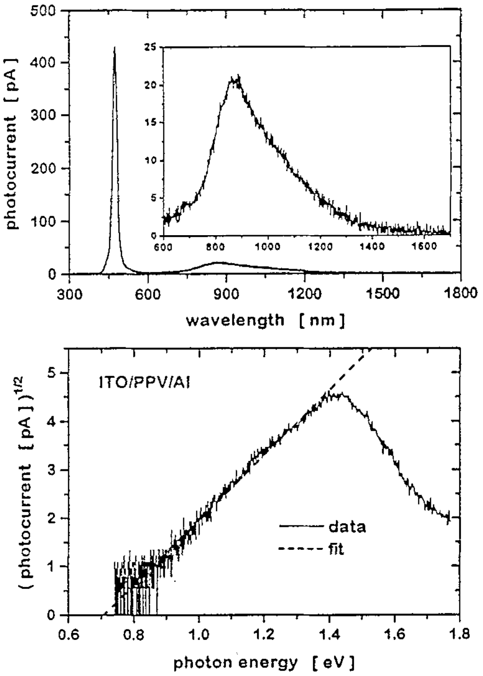


*Fig. 2: Photoaction spectra of ITO/PPV/Al devices with illumination through the ITO; the lower graph shows the determination of the barrier height by extrapolation to the energy axis*

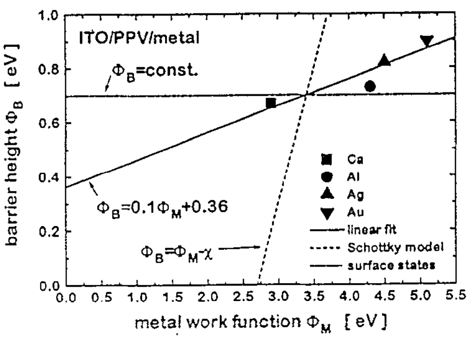


*Fig. 3: Dependence of the experimentally determined barrier height on the metal work function*

### 3. Thermally Stimulated Currents

Another important factor for understanding the physical behaviour of polymer-based light emitting devices is the presence of trap states for charge carriers. A classical method for the determination of the energetic depth of these states in inorganic semiconductors is the measurement of thermally stimulated currents (TSC).[9] We have used this technique to investigate trap states in PPV light emitting devices. In the experiment the sample is cooled to an initial temperature of about 10K. At this temperature the traps are filled by applying a current for a certain period of time. Finally, while the sample is heated up to room temperature at a constant heat rate of several K/min the discharge current without bias is recorded as a function of temperature. When charge carriers are thermally detrapped peaks in the TSC spectra occur at a certain temperature. From the position and form of these TSC maxima the energetic depth of trap states can be determined.

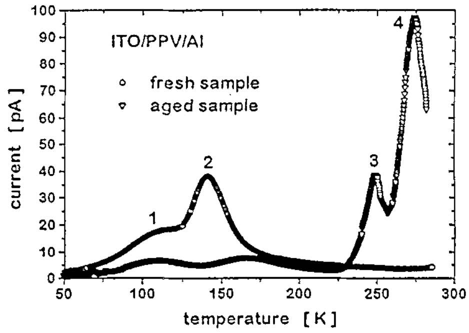


*Fig. 4: Thermally stimulated currents in ITO/PPV/Al devices*

Fig. 4 shows typical TSC spectra of two ITO/PPV/Al devices (one measured under vacuum and the other one after storage in air). The spectra show four distinct peaks in the temperature range between 50 and 300K with trap energies of about 0.1eV (1), 0.2eV (2), 0.8eV (3) and 0.9eV (4), respectively. The comparison of the fresh and aged sample shows that storage under ambient conditions creates deep traps, whereas the intrinsic trap states in PPV are rather shallow. For a detailed understanding of the chemical nature of the traps, further investigations are necessary.

### 4. Conclusion

Investigations of metal-polymer barriers in PPV LEDs with internal photoemission show that there is a significant influence of surface and interface states, which lead to a very weak dependence of the barrier height on the metal work function. With thermally stimulated currents we have detected shallow and deep trap states, depending on the sample preparation. Further investigations are in progress in order to get a better understanding of charge carrier injection and transport in these polymer LEDs.

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