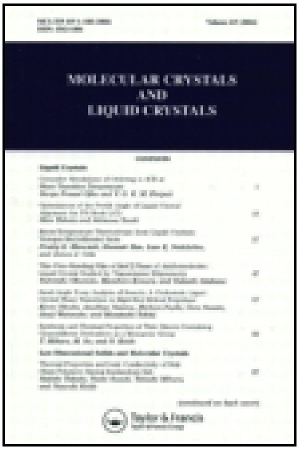

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ELECTRICAL AND OPTICAL CHARACTERIZATION OF LIGHT EMITTING POLY-PHENYLENE-VINYLENE DIODES

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Abstract We investigated the electrical and optical properties of light emitting devices based on poly-p-phenylene-vinylene (PPV). At room temperature I-V-characteristics in the dark reveal a good diode behaviour with a maximum rectification ratio of 10^6. The threshold voltage for visible electroluminescence (EL) is device dependent and under best conditions we measure values as low as 2 V forward bias. At low temperatures the rectification ratio is considerably smaller and EL can be observed in both current directions. Impedance measurements show that at room temperature our diodes can be described within the Schottky barrier model as a serial circuit of resistive and capacitive components. Aging experiments point to a significant influence of air on the electrical properties and consequently on the lifetime of the devices.

INTRODUCTION

Electroluminescence in organic materials goes back to 1963 with its observation in anthracene crystals by Martin Pope (for a review see [1]). Molecular compounds are considered as applicable in light emitting devices because of their high fluorescence efficiency and the wide range of possible emission colours [2, 3]. With the discovery of EL in PPV [4] a new research interest in the semiconducting properties of conjugated polymers arose [5, 6].

Polymeric materials display a fluorescence efficiency almost as high as molecular dyes and adjusting the polymer backbone also produces a wide range of energy band gaps, which spans the visible spectral range. Furthermore the addition of side groups offers possibilities such as solubility and processability, both properties essential for application of these materials in electronic devices. Meanwhile light emitting diodes (LEDs) with impressive efficency, brightness and uniformity in various colours have been manufactured. Flexible light emitting structures and solar cells [7, 8], which take unique advantage of the processing techniques and mechanical properties of polymers suggest new opportunities for new device properties and performance. In this paper we present a brief characterization of the electrical properties of PPV - based LEDs.

SYNTHESIS OF PPV AND DEVICE FABRICATION

PPV is **insoluble** and unmeltable like most other conjugated polymers. Therefore it is synthesized via a precursor polymer route [4, 9]. The soluble precursor polymer shows an excellent processability and homogeneous, dense films with areas of 20×15 cm^2 can be prepared with a doctor blade technique. Spin-coating is also possible. The thickness of these films is controllable in a wide range between **ca.** 100 Å and 100 μm.

The conversion of the precursor polymer to PPV is made by heating under vacuum. The conditions during this thermal elimination are essential for the purity of the polymer films and hence for the electrical and optical properties of the devices. Data from elementary analysis show that under best conditions the impurity concentration is less than 0.5 % [7]. Thermogravimetric analysis proves that PPV is a thermally and long time stable polymer. In the absence of air it is resistant up to 400°C [9].

PPV is an organic semiconductor with an energy gap of about 2.5 eV. As shown in detailed investigations from the Cambridge group [10], the gap can be tuned via the synthesis of co-polymers by about 0.5 eV, which allows a variation of the colour from yellow-green to red.

LEDs based on conjugated polymers are commonly fabricated in a Schottky diode configuration which for example consists of a p-type semiconductor with two different metal electrodes. An ohmic contact is formed at the interface between the metal with the higher workfunction and the semiconductor. A rectifying junction establishes at the contact between the semiconductor and the metal with the lower workfunction.

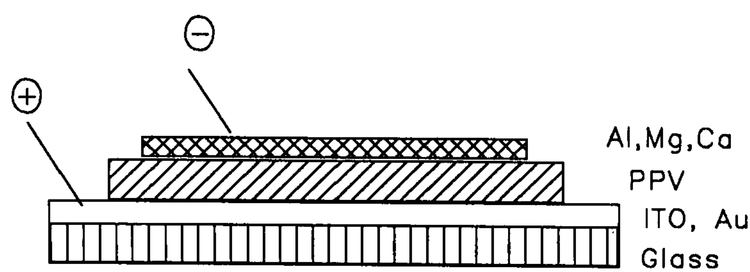

FIGURE 1: Sandwich configuration of a light emitting Schottky-barrier device, prepared by coating a glass/ITO substrat with the PPV-precursor and subsequent thermal conversion. The vacuum evaporated top metal contact (Al,Mg or Ca) gives the rectifying junction.

Our devices are fabricated in a sandwich configuration (Figure 1) with ITO or Au as the transparent ohmic contact, the fully converted PPV layer (thickness 0.1 -

1 μm) and a rectifying electrode of Al, Mg or Ca [4, 9]. The rectifying electrode was evaporated on the polymer at a pressure below 10^{-2} Pa.

The typical device size used in our studies is 0.1 cm^2, but due to the good processability of PPV the fabrication of large LEDs is possible and our largest devices have active areas of more than 2 cm^2.

DEVICE CHARACTERIZATION

I-V-characteristics and Electroluminescence

In Figure 2 dark current and EL intensity versus bias voltage of an Al/PPV/ITO device are drawn. The I-V-characteristic is asymmetrical and reveals a good diode behaviour. Typical rectification ratios of our diodes lie between 10^4 and 10^6. In the range of 1 - 2 V forward bias voltage V_F the current follows approximately an exponential dependence according to the standard equation

$$I = I_0(\exp(qV_F/nk_BT) - 1)$$

where q is the electronic charge, n the ideality factor and k_B the Boltzmann constant. From the semilogarithmic representation (see insert of Fig. 2) the ideality factor

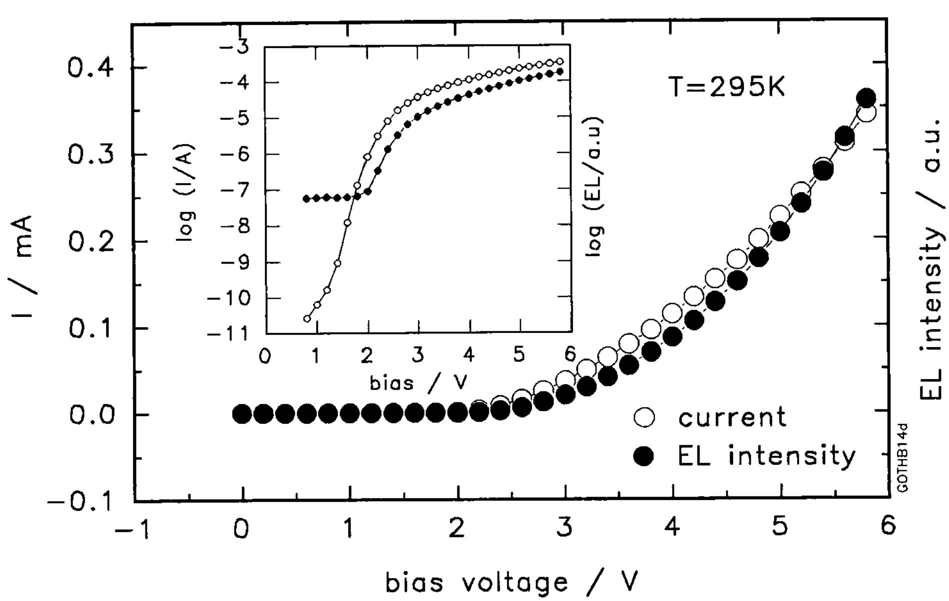

FIGURE 2: I-V-characteristic and EL intensity versus applied bias voltage of an ITO/PPV/Al device (thickness 0.2 μm). Visible EL appears significantly below 2.5 V. The insert shows the semilogarithmic representation.

can be calculated as 3.5, significantly larger than unity as expected by different theories [11]. Possible explanations for this behaviour are the influence of a serial bulk resistance and the role of an interfacial oxide layer between PPV and the metal electrodes (see for example [12]).

Depending on the semiconducting properties of PPV, the film thickness, the rectifying electrode material and the conditions during device fabrication visible EL appears at room temperature at voltages exceeding a threshold of at least 2 V forward bias in our best devices. Figure 2 displays the correlation between I-V-characteristics and emission intensity, the first response of the photomultiplier occurs at a current density of about 10 $\mu A/cm^2$.

In figure 3 EL-spectra at room temperature and 4K, together with the photoluminescence (PL) spectrum and the optical absorption are shown. The measured PL and EL spectra in these devices are essentially equal, indicating that the same exited states are involved. In the emission spectra several vibronic peaks of the exciton series appear, moderately broadend by phonons [13]. The zero-phonon line is located close to the absorption edge and probably affected by re-absorption of the bulk material because the emission is observed through the bulk material.

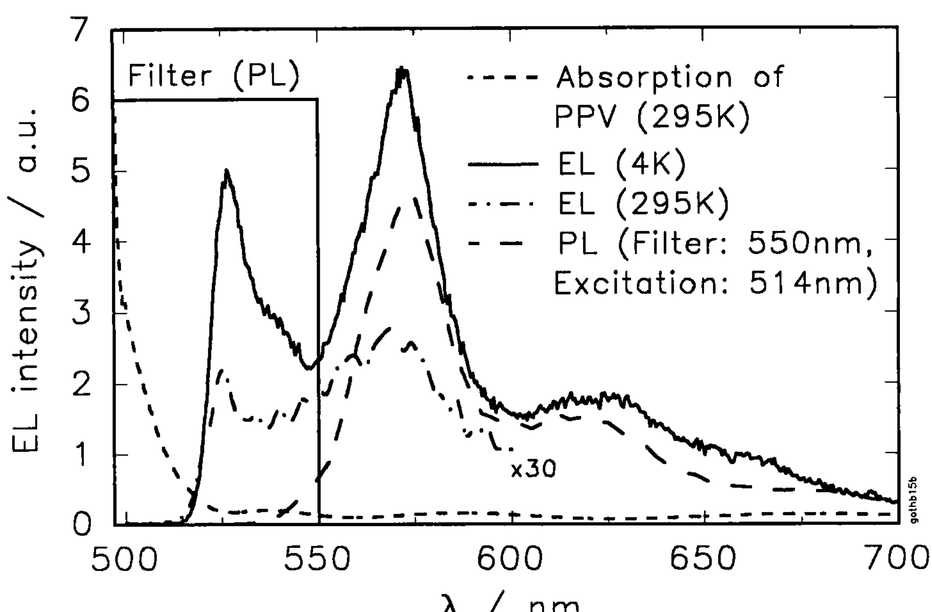

FIGURE 3: Emission spectra of EL and photoluminescence of an Al/PPV/ITO device. For comparison the absorption spectrum of PPV at room temperature is also displayed.

Detailed investigations of the temperature dependence of our devices reveal drastical changes of the electrical properties. At constant current the intensity of EL in liquide helium is about two orders of magnitude higher than at room temperature. However the threshold voltage for visible luminescence increases significantly, on our devices by typically one order of magnitude from room temperature to 4 K. I-V-characteristics of an AL/PPV/ITO device and symmetrical structures are shown in figure 4. With decreasing temperature the rectification ratio of the Al/PPV/ITO device decreases and at 77 K the I-V-characteristic shows no distinct diode behaviour. An equal shape of the characteristics is also observed in the symmetrical devices (Au/PPV/Au, Al/PPV/Al) at liquid nitrogen temperature. All our devices investigated, even the Al/PPV/ITO devices, show EL in both current directions at low temperatures, however at high electrical threshold voltages.

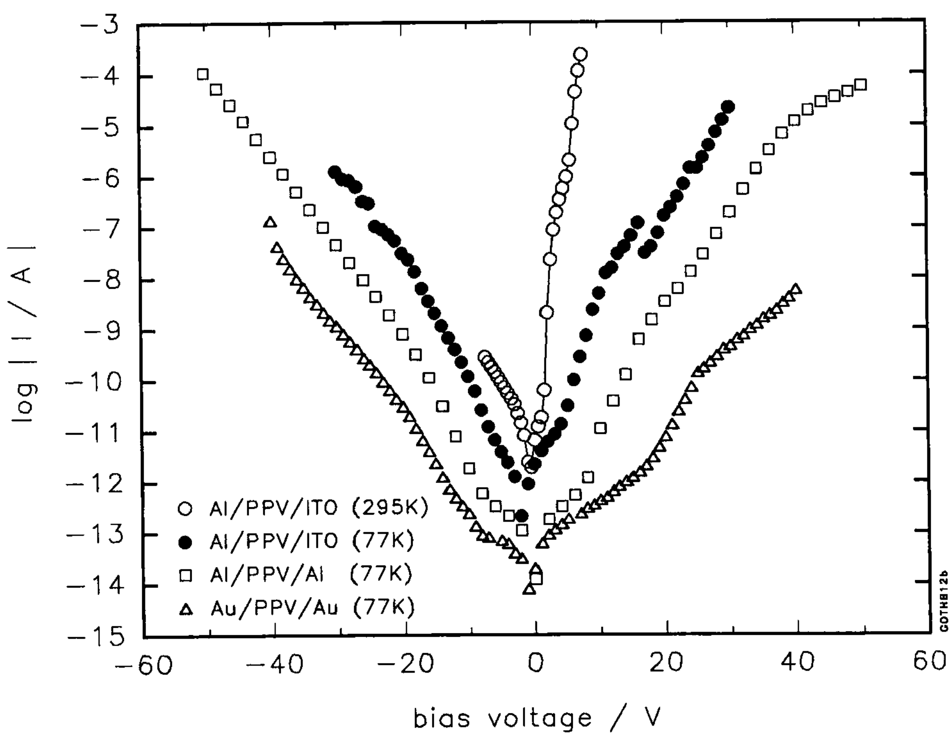

FIGURE 4: I-V-characteristics of an AL/PPV/ITO device (○: 295K; •: 77K) and symmetrical structures of Au/PPV/Au (△: 77K) and Al/PPV/Al (□: 77K).

These results indicate that the Schottky junction no longer exists and is consequently not essential for EL at low temperatures. Hence a Schottky barrier is essential for light emission at low voltages at room temperature, however it is not fundamentally necessary for EL in conjugated polymers.

Impedance spectroscopy

Figure 5 shows real and imaginary parts of the complex impedance of an ITO/PPV/Al device for different applied bias voltages at room temperature. Commonly the frequency dependence of Schottky barrier diodes can be simulated by the equivalent circuit shown in the insert of figure 5. C_j and R_j characterize the junction and C_b and R_b represent the undepleted bulk. The complex plane representation of this equivalent circuit yields two perfect semicircles with diameters corresponding to the ohmic resistances. In our case all quantities are field, frequency and temperature dependent, giving deviations from this ideal form.

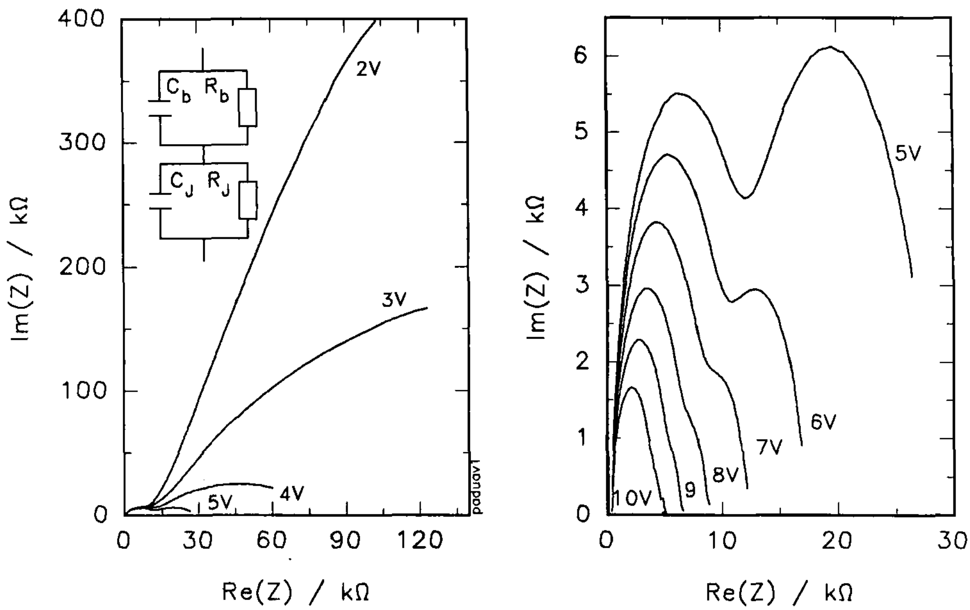

FIGURE 5: Impedance plots at room temperature of an Al/PPV/ITO device (thickness: c. 1 μm) under different forward bias. The insert shows the equivalent circuit.

The right arc belongs to the layer with the greater capacitance, the diameters of the semicircles correspond to the ohmic resistances. At low bias the resistance of the diode is dominated by the rectifying junction represented by the right branch. With increasing forward bias the resistivity of the junction decreases and at high bias (10 V) only the bulk remains. From the junction capacitance dependence of reverse bias intrinsic device parameters such as ionized acceptor dopant concentration, diffusion voltage and width of the depletion layer can be obtained [7]. Further practical applications of the impedance spectroscopy are investigations of the resistance and capacitance as functions of temperature or aging [8].

Aging Experiments

Technical applications of the devices imply long term stability. In Figure 6 impedance plots of a two months old device stored at laboratory conditions are shown. Impedance measurement was performed at room temperature under 6 V forward bias during evacuation.

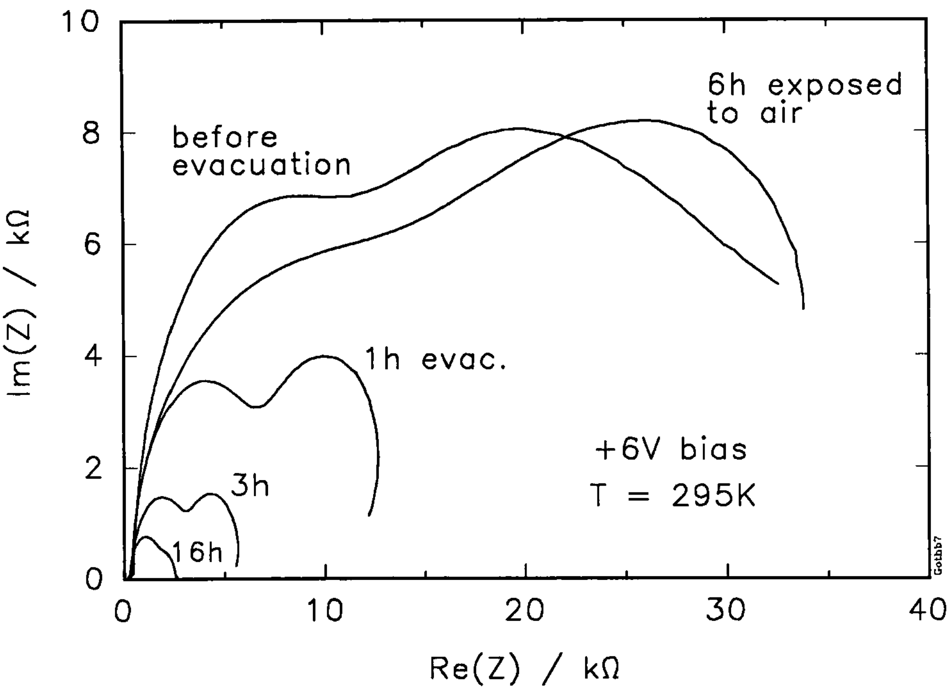

FIGURE 6: Impedance plots of a two months old Al/PPV/ITO device at room temperature during evacuation (10^{-3}Pa) and subsequent exposure to air.

Before evacuation we observe two large semicircles corresponding to high resistances of both bulk and junction and visible EL appears at about 6 V. During evacuation an enormous decrease of both resistances occurs and after 16h the device behaves almost like a just prepared diode and visible EL is observed at about 4 V. Exposing the device to air again, both semicircles increase and also the threshold for EL (c. 6 V again).

This experiment shows that storage on air causes no irreversible changes in the device, however it affects drastically the electronic properties. A lower resistance respectively a lower voltage causes less heating and stress for the device and hence a longer lifetime.

CONCLUSIONS

Impedance spectroscopy shows that at room temperature Al/PPV/ITO devices can be described by a simple equivalent circuit for the Schottky barrier model. The Schottky junction leads to a good diode behaviour and is essential for the observed photovoltaic effect [7, 8] and the low threshold voltage for EL. With decreasing temperature the ionized acceptor dopant concentration gradually freezes out and the Schottky barrier vanishes. Aging experiments reveal a significant influence of air on the electronic properties of the devices. Lifetime and efficiency of the light emitting diodes can be increased by avoiding contact with air.

ACKNOWLEDGEMENTS

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