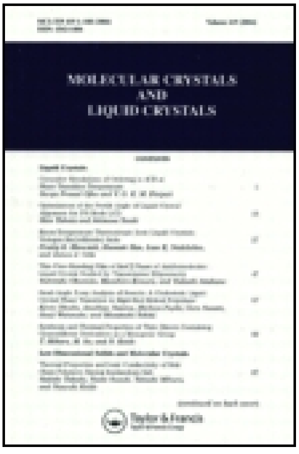

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MetaVInsulatorPolymer - LEDs Based on PPV

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METAL/INSULATOR/POLYMER - LEDs BASED ON PPV

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Abstract We investigated the current-voltage (I-V) and electroluminescence (EL) characteristic of metal/polymer and metal/insulator/polymer (MIP) LEDs based on poly (1,4-phenylene vinylene) (PPV). The I-V- and EL characteristics of the MIP structures display a pronounced dependence of the insulator thickness and we measure an increase of the quantum efficiency of more than a factor of 40 at an AlO_x layer thickness of 3-5nm. The device characteristic is qualitatively understood within inorganic metal/insulator/semiconductor (MIS) theory and can be explained by a voltage dependent barrier for minority carrier injection in connection with a hole blocking barrier at the PPV/insulator interface. With MIP structures we reveal external quantum efficiencies up to 0.01%, comparable to values achieved on monolayer Ca LEDs. The MIP structures, however have the advantage, that a more stable device performance is obtained.

INTRODUCTION

The conjugated polymer PPV and its derivatives are since the discovery of EL by Burroughes [1] object of tremendous interest[2,3] in order to use them as active material in polymer light emitting diodes (PLEDs). PPV is distinguished by excellent film forming properties, high photoluminescence quantum efficiencies (10-30%) and a good chemical and thermal stability, which are presuppositions for the fabrication of efficient and long term stable PLEDs. Until now monolayer LEDs based on PPV have been fabricated with active areas of more than $50cm^2$ - even on flexible substrates - , offering the prospect for new technical applications.[4] The onset voltage of our monolayer devices can be below 2V and an operating time of more than 2100h is promising.[5] A drawback however, is the relative low quantum efficiency, due to poor electron injection. For efficient EL, however a balanced injection is important. In order to improve the minority carrier injection we have fabricated MIP structures.

CHEMISTRY AND DEVICE FABRICATION

Poly (1,4-phenylene vinylene) is prepared by the sulphonium prepolymer route. Details of our chemical synthesis, film- and device preparation are presented elsewhere.[5,6,7] The MIP structures were fabricated by evaporating a thin Al layer at a pressure of about 10^{-6} mbar onto the PPV film, and a subsequent heating process at 120°C under ambient conditions for 2h, in order to convert the thin Al layer into an AlO_x layer. The thickness of the thin interfacial layer was measured during the evaporation process via a sensor placed near the sample position; typical evaporation rates were 0.5-1Å/s. To allow a direct comparison between monolayer and MIP devices all samples were fabricated from the same batch and even the monolayer LEDs without AlO_x layer were heated at 120°C for 2h under ambient conditions.

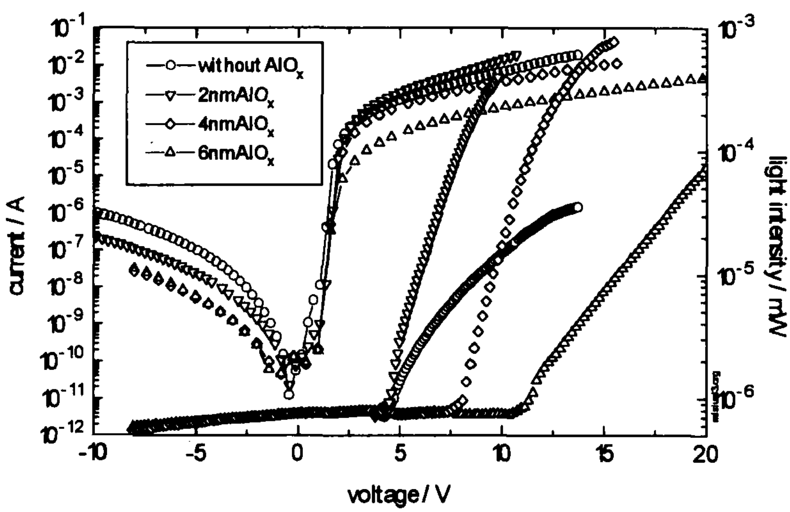

FIGURE 1 I-V- and EL-V-characteristics of different ITO/PPV/AlO_x/Al LEDs

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 presents the I-V-characteristics of ITO/PPV/AlO_x/Al LEDs for various thick AlO_x layer, ranging from 0 to 6nm. The monolayer device (ITO/PPV/Al) with no intentionally prepared oxide layer, displays a Schottky diode behaviour with an exponential current rise in forward direction. A detailed description of the device characteristics of monolayer LEDs can be found in.[7] In comparison to the monolayer LEDs the MIP structures display a slightly different behaviour. With increasing insulator thickness the current in reverse direction gradually decreases. In forward direction the current flow is also reduced, especially the dynamics of the exponential current rise is diminished for more than one order of magnitude, being indicative for a larger serial resistance R_S. Compared with the I-V-characteristics, the EL - voltage (EL-V) behaviour shows more drastic changes. In forward direction, the monolayer diode displays an onset for EL of about 3.5V, typically we measure 1.6 to 4V for different devices. The EL-V characteristic is smooth and consequently the achievable brightness low. In contrast, the 2nm MIP structure displays a steep EL rise at a similar onset voltage. Even at higher current densities, the characteristic is steep and no significant flattening of the EL-intensity is observed. With increasing oxide layer thickness the onset for EL enlarges (4nm: 7.5V), the overall characteristic, however shows a similar behaviour. At an insulator thickness of about 6nm the threshold is shifted to 11V and the EL-V curve becomes flat again. No significant EL before dielectric breakdown is achieved at an insulator thickness of more than 10nm.

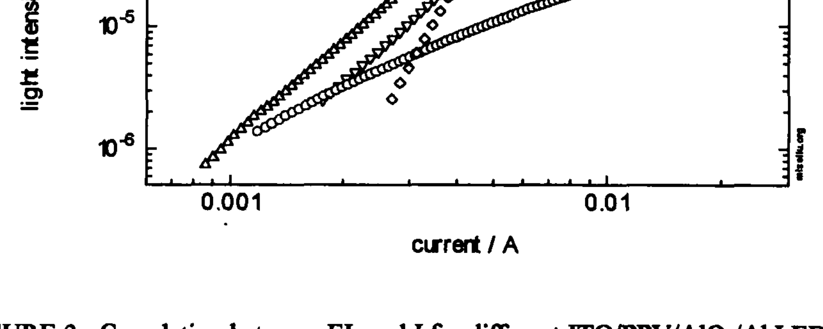

FIGURE 2 Correlation between EL and I for different ITO/PPV/AlO_x/Al LEDs

The correlation between current and EL of these devices is displayed in Figure 2. This plot depicts the different functional dependencies of the devices as well as the improved minority carrier injection of the MIP structures. While the monolayer devices display an approximately linear behaviour of EL versus I, the MIP LEDs show an EL $\propto I^{\alpha}$ with $\alpha \approx$ 2-3, leading to an enhanced quantum efficiency of the MIP structures at higher current densities. For example, in comparison to the normal Schottky diodes, the 4nm MIP structure displays a light output, which is enhanced for a factor of ≈ 40.

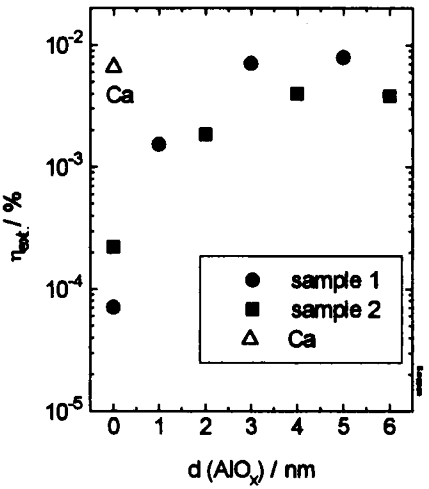

FIGURE 3 External quantum efficiencies of ITO/PPV/AlO_x/Al LEDs in dependence of the AlO_x layer thickness. A maximum of the quantum efficiency is measured at 3-5nm insulator thickness, comparable to Ca LEDs.

The quantum efficiency as a function of the insulator thickness of the above mentioned devices and reference samples are presented in Figure 3. For comparison, we also show data for a Ca monolayer LED, prepared from the same polymer batch. This plot clearly reveals, that a maximum of EL quantum efficiency is observed as a function of layer thickness. In our case, both samples show a maximum, which occurs at an insulator thickness ranging between 3 and 5 nm. The difference in light output between the two batches reflects the scattering of EL of nearly identically fabricated devices and points to the very sensitive reaction of minority carrier injection to slightly different preparation conditions. The above described increase of quantum efficiency via an insulating layer is a well known phenomenon from inorganic Schottky diodes. In the case of crystalline inorganic MIS diodes the enhancement of quantum efficiency can be explained within the energy band model. We are well aware, that the charge carrier injection and transport processes in polymeric devices are much more complex, however classical band model theory can give at least a qualitative understanding of the processes found in polymeric LEDs. Crucial for the changing of the minority carrier injection ratio in MIS-structures is the voltage drop over the insulating layer, which cause a relative shift of the conduction (E_C) and the valence band (E_V) of the semiconductor opposite to the Fermi level of the metal E_{FM} (see Figure 4, V= 0 and V>0).

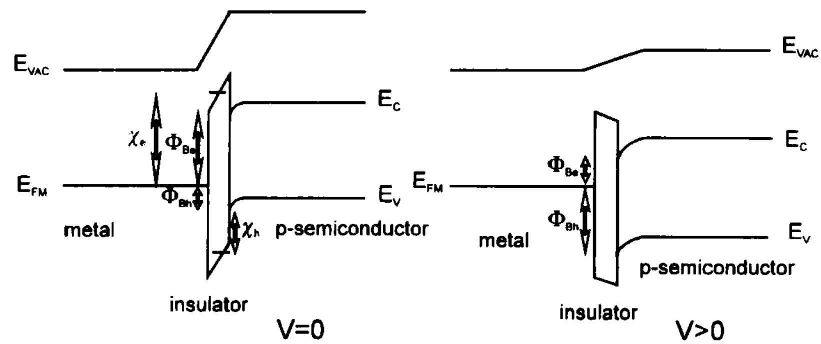

FIGURE 4 Bandpicture of an inorganic metal/insulator/p-type semiconductor (MIS) structure with and without bias (V>0, V=0).

This shift can lead to a diminished barrier for minority carrier injection (Φ_{Be}) and an increased majority carrier barrier (Φ_{Bh}). Furthermore the average barrier heights for the tunnel current (χ_h, χ_e) can be changed. These barrier heights, together with the finite insulator thickness d lead to the appearence of a tunnelling term in the quantitative description of the I-V-curve for MIS-diodes (see Equation 1). The tunnel current of majority charge carriers is given by:

$$I = I_0 \exp\left(-\sqrt{\chi_h}d\right)\exp\left(\frac{qV}{nkT} - 1\right) \qquad (1)$$

A similar equation is obtained for the minority charge carriers. The tunnel term $\exp\left(-\sqrt{\chi_{h/e}}d\right)$, characteristic for both types of charge carriers, disappears for an insulator thickness $d \rightarrow 0$ and Equation (1) reduces to the Shockley equation.[8] For $d \rightarrow \infty$ no tunnelling of charge carriers is possible. Between these to two extrema, there exists an optimum layer thickness *d*, at which an enhanced minority carrier injection occurs. For a detailed description of MIS structures see for example Card and Rhoderick.[9] The described behaviour leads to an insulator thickness dependence of the light output, which is detected on our MIP LEDs (see Figure 3.). The insulating layer has the task to modify the energy levels for electron injection on one hand, on the other hand, it should block the majority carrier flow. These criteria cannot be fulfilled with every insulator. For example, our investigations on ITO/PPV/SiO_x/Al MIP structures have revealed, that these devices display a similar I-V-characteristic as displayed in Figure 1, however a significant drop of light output, indicating that the minority carrier injection was reduced because of unfavourable χ_h and χ_e values.

SUMMARY

In this paper we have reported on an enhancement of the quantum efficiency of PPV LEDs by fabricating MIP structures. The MIP LEDs consist of an additional thin AlO_x and displays a pronounced insulator thickness dependence of the quantum efficiency. The I-V - characteristics as well as the thickness dependent quantum efficiency can be qualitatively understood within inorganic MIS theory. A maximum of light output is detected at an AlO_x thickness ranging between 3 - 5nm, achieving external quantum efficienies comparable to monolayer Ca devices. In comparison to Ca LEDs the MIP structure are distinguished by an enhanced lifetime.

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