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Multilayer Organic Light Emitting Diodes for Efficient Carrier Injection and Confinement

Dirk AMMERMANN, Achim BÖHLER, Siegfried DIRR and Wolfgang KOWALSKY

Institut für Hochfrequenztechnik, TU Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany

Organic light emitting diodes (OLEDs) grown by the organic molecular beam deposition (OMBD) technique achieve bright electroluminescent emission in the blue and green spectral region. Low turn-on voltages and high luminous efficiencies are obtained with complex multilayer structures and a novel starburst molecule used for improved hole injection. The electrical and optical characteristics of different green and blue emitting devices with Alq_3 and OXD-8 as emitter material, respectively, are compared.

1. Introduction

Electroluminescent devices based on organic semiconductors (OLEDs) offer a promising low-cost alternative to conventional emissive flat panel displays. After the first demonstration of a green emitting OLED in 1987 by Tang and VanSlyke[1], numerous organic dye molecules for electroluminescence in the entire visible spectral region have been investigated[2]. A significant improvement in quantum efficiency is obtained with multilayer devices. The double heterostructure[3] commonly used for inorganic semiconductors with separate electron and hole transport layers allows to confine both charge carriers and excitons within an emitter layer sandwiched between the transport layers. The choice of the emitter molecule determines the emission wavelength.

2. Device Structures

Fig. 1 shows the layer sequences of different multilayer devices with light emission in the blue and green spectral region. The device efficiency is mainly determined by the injection process at the electrodes and by the confinement of charge carriers and excitons within the emission layer.

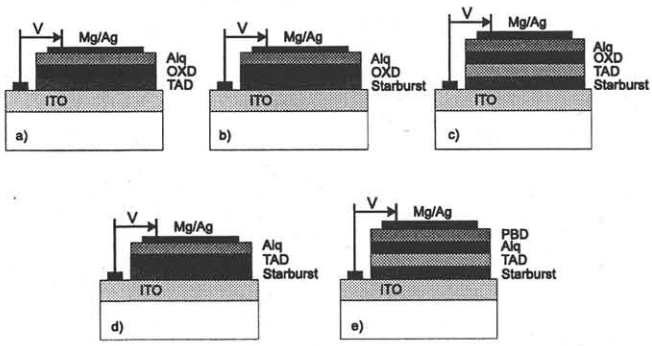

Fig. 1: Multilayer organic light emitting diodes for the blue (a-c) and green (d-e) spectral region.

The energy level diagram (Fig. 2) illustrates the principle of operation of a modified double heterostructure device. Electrons are injected from a low work function Mg contact protected by a Ag layer from atmospheric oxidation. In contrast to conventional double heterostructure devices, an additional hole injection layer is inserted between the ITO contact and the hole transport layer to lower the barrier and to improve the device performance. Electrons and holes are confined within the emitter layer and recombine creating excitons followed by a radiative decay for light emission. The multilayer structure also allows to confine excitons and to avoid non-radiative decay paths, e. g. contact quenching, in order to obtain higher luminous efficiencies.

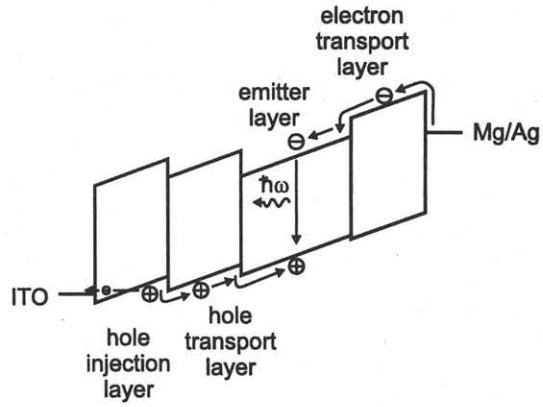

Fig. 2: Energy level diagram of a multilayer OLED with hole injection and transport layer.

3. Organic Materials and Device Fabrication

The molecular structures of the organic materials are shown in Fig. 3. Preferentially hole transporting behavior is observed for TAD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine) and the triphenylamine-derivative starburst molecule. PBD (2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3-4-oxadiazole) and Alq_3 (tris-(8-hydroxychinoline) aluminum) serve as electron transport materials. The metal chelate complex Alq_3 is also known for its high fluorescence yield in the green spectral region. Blue emitting electroluminescent devices are fabricated using OXD-8 (1,3-bis(N,N-dimethylaminophenyl)-1,3,4-oxadiazole) as emitter molecule[4]. In addition to organic dye molecules, rare-earth (RE) complexes are very promising candidates for light emission in the visible spectral region. OLEDs with an $Eu(TTFA)_3Phen$ (europium-tris(1-thenoyl-3-trifluoracetonate)-1,10-phenanthroline) emitter layer[5] show emission in the red spectral region with

narrow spectral bandwidth. The organic thin films are grown onto ITO-coated glass substrates by the organic molecular beam deposition (OMBD) technique under ultrahigh vacuum conditions at growth rates of about 2-8 nm/min[6]. Metal thin films for electron injection are evaporated from tungsten or molybdenum boats. The contacts consisting of 120 nm Mg and 120 nm Ag are laterally defined by a shadow mask with 2 mm diameter circular holes.

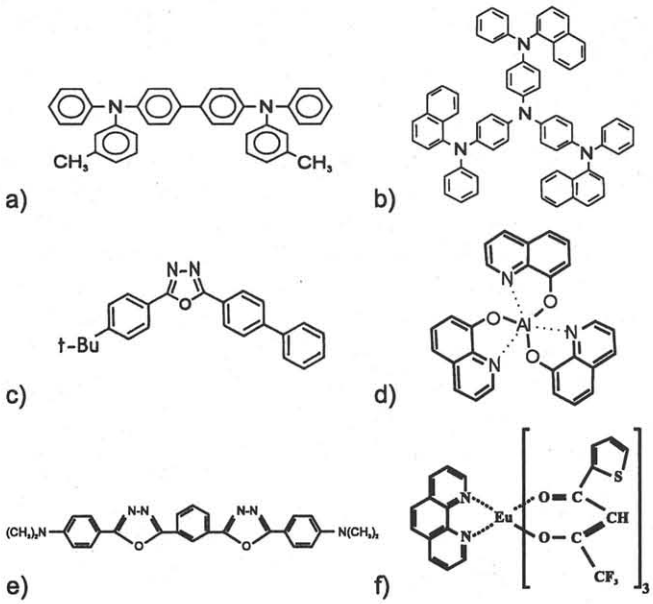

Fig. 3: Molecular structures of (a) TAD, (b) Starburst molecule, (c) PBD, (d) Alq_3, (e) OXD-8, and (f) $Eu(TTFA)_3Phen$.

4. Organic Light Emitting Diodes

For device characterization, current-voltage and luminance(optical power)-current characteristics are recorded for cw-operation and at normal atmospheric conditions and room temperature. The luminance was measured with a Minolta LS-110 luminance meter. A calibrated large-area Si photodetector (Advantest) was used to determine the optical output power. The internal quantum efficiency of the devices is estimated from the ratio of light generated within the structure to the light detected by a photodetector with limited aperture. Only about 11 - 15 % of the total emission is measured due to Fresnel transmission losses, absorption, and total reflection at the interfaces. The luminous efficiency takes into account the spectral intensity distribution with respect to the human eye response measured with the luminance meter.

The electroluminescence spectra were recorded with a 200 mm monochromator. Bright blue and green electroluminescence with peak wavelengths of 462/475 nm and 520 nm, respectively, was observed under cw-operation at room temperature and normal ambient conditions (Fig. 4).

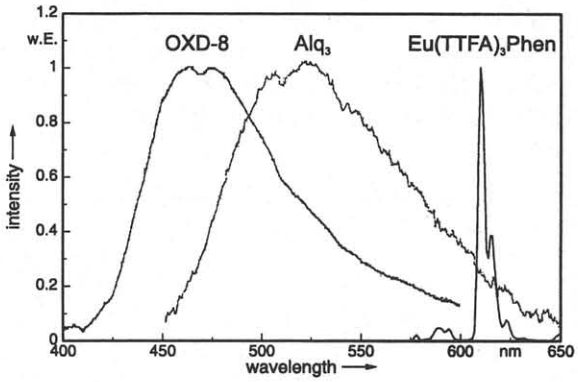

Fig. 4: Electroluminescence spectra of blue and green OLEDs. The photoluminescence spectrum of $Eu(TTFA)_3Phen$ is also shown.

Due to radiative transitions of the Eu^{3+} ion, the spectral bandwidth of the red emitting $Eu(TTFA)_3Phen$ complex is only 5 to 10 nm compared to about 80 nm for the dye molecules.

Three different double heterostructure blue emitting diodes were fabricated to investigate the effect of the hole injection layer (Fig. 1a-c). The current-voltage and luminance-current characteristics of OLEDs with 20 nm Starburst or TAD (15 nm Starburst and 5 nm TAD, respectively), 30 nm OXD-8, and 20 nm Alq_3 are shown in Fig. 5. The turn-on voltage and the luminous efficiency are already improved for an OLED with the Starburst molecule as hole transport material compared to the standard TAD device. The combination of Starburst hole injection and TAD transport layers allows both to achieve turn-on voltages below 7 V and to increase the quantum efficiency. An improvement with respect to turn-on voltage (10 V, 8 V, and 7 V, respectively), estimated internal quantum efficiency (2.2 %, 3.3 %, and 4.3 %), and luminous efficiency (0.3 lm/W, 0.5 lm/W, and 0.8 lm/W) is deduced from the characteristics.

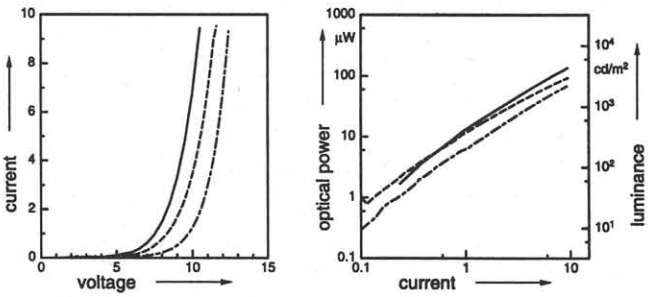

Fig. 5: Current-voltage and luminance-current characteristics of the blue emitting device with different hole transport layers: Starburst/TAD (—), Starburst (- -), and TAD (- · -).

The energy level diagram (Fig. 2) allows to explain the results. Holes injected into the TAD layer are efficiently transported to the emitter layer, however, the injection from the ITO electrode is limited by a large energy barrier. In contrast, holes can easily be injected into the

Starburst layer. The insertion of the TAD hole transport layer between the Starburst hole injection and the OXD-8 emitter layer reduces the energy barrier encountered at the Starburst/OXD-8 interface. The staircase-like HOMO level sequence provides an efficient hole injection and transport path and improves the device performance.

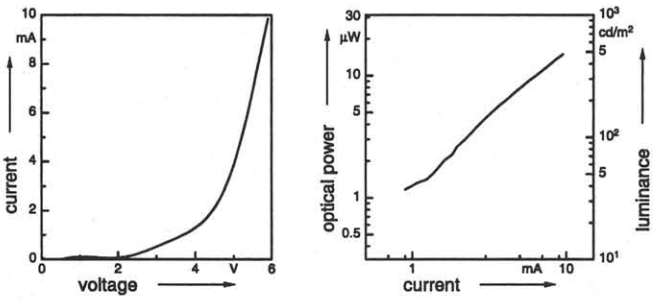

Fig. 6: Current-voltage and luminance-current characteristics of the green emitting device.

The current-voltage and luminance-current characteristics of the green single heterostructure OLED (Fig. 1d, 15 nm Starburst, 5 nm TAD, 20 nm Alq_3) are shown in Fig. 6. The low turn-on voltage of about 4 V is traded off for a decrease in quantum efficiency. An improvement in efficiency by a factor of more than 5 is found for a 50 nm thick Alq_3 layer, however, the turn-on voltage is about 9 V. Typical luminous and internal quantum efficiencies are about 1 lm/W and 5 %, respectively. The insertion of a separate electron transport layer, e. g. PBD, also improves the device performance significantly[7].

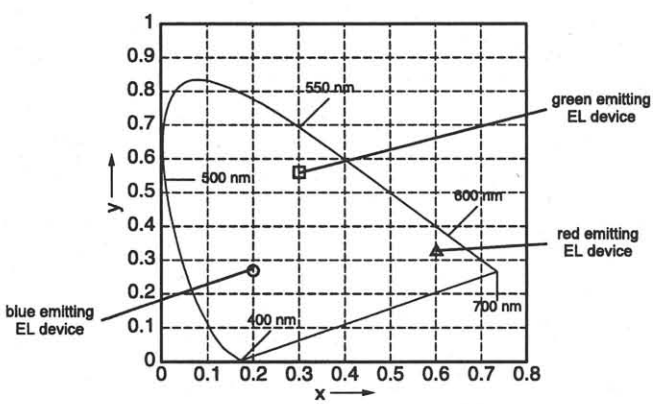

Fig. 7: Chromaticity diagram with CIE coordinates of the blue, green, and red emitting electroluminescent devices.

5. Flat Panel Display Applications

Multilayer organic light emitting diodes have the ability to compete with other emissive technologies, e. g. plasma, vacuum fluorescence, or inorganic thin film electroluminescence displays. A luminance exceeding 100-1000 cd/m^2 and a luminous efficiency of 1-2 lm/W to 5 lm/W required for indoor and outdoor flat panel applications[8], respectively, are possible. Low information content displays, e. g. alphanumeric displays, or sign boards, can be fabricated by photolithographic definition of contact patterns or OLED structures. Lightweight and flexible polyaniline (PANI) substrates are suitable for organic electroluminescent displays and offer a large potential for applications.

The color perception of the blue, green, and red emitting OLEDs is summarized in the chromaticity diagram shown in Fig. 7. The emission color can be varied over the entire visible spectral region by choosing appropriate dye molecules.

6. Conclusions

Charge carrier injection and confinement are crucial for organic light emitting diodes (OLEDs) with low turn-on voltages and high luminous and internal quantum efficiencies. Multilayer structures with separate hole injection, hole transport, emitter, and electron transport layers allow to achieve bright emission in the blue and green spectral region. In addition, the device performance was improved using a novel Starburst molecule as hole injection material.

Blue emitting devices based on OXD-8 showed turn-on voltages of about 7 V, luminous and internal quantum efficiencies of 0.8 lm/W and 4.3 %, respectively. Turn-on voltages of only about 4 V were achieved with Alq_3 based green emitting devices.

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