Multilayer Organic Light Emitting Diodes for Flat Panel Displays

Dirk Ammermann, Achim Böhler, Wolfgang Kowalsky

Organic light emitting diodes (OLEDs) are attractive for the use in lightweight, low-cost flat panel displays. Multilayer devices grown by the organic molecular beam deposition (OMBD) technique achieve bright electroluminescent emission in the entire visible spectral region. Turn-on voltages below 10 V, luminances of about 10^4 *cd/m*^{2}*, and internal quantum efficiencies exceeding 5 % are satisfactory for emissive displays. In this paper, we describe the OLED fabrication technology and present results for blue and green emitting devices. Different multilayer structures are proposed and compared with respect to their electrical characteristics and quantum efficiencies.*

1 Introduction

Flat panel displays have obtained a significant and still growing share of the display market. Their advantages, i. e. low power consumption, light weight, and small size, as compared to conventional cathode ray tubes (CRTs), have led to a large number of applications. However, severe drawbacks of the most widely commercialized product, liquid crystal displays (LCDs), limit the success of this technology. In particular, the narrow viewing angle, a bright backlight necessary in dark environments, and the high fabrication costs for large area displays are major problems to be solved. Emissive display technologies may overcome these disadvantages. Although conventional LEDs for the visible spectral region based on III-V semiconductors (InGaN, AlInGaP) achieve bright emission with sufficient quantum efficiency, their use for flat panel displays is unlikely due to the high fabrication and packaging costs for mounting individual devices in a 0.2 mm array or for the monolithical integration on a single substrate.

In addition to inorganic semiconductors, a new class of materials has attracted research interest during the last decade. Organic semiconductors show good charge carrier transport properties as well as high luminescence efficiencies of nearly 100 %. Since the first demonstration of a green organic light emitting diode (OLED) in 1987 by Tang and VanSlyke [1], numerous organic molecules and polymers have been found that exhibit electroluminescence in the blue, green, and red spectral region [2, 3]. Polymer-based OLEDs are usually fabricated by spin-coating techniques whereas small dye molecules are preferably vapor-deposited under ultrahigh vacuum conditions. The latter technology is not only compatible with the epitaxial growth of inorganic semiconductors but also allows to precisely control the layer thickness and morphology and to prepare complex multilayer structures [4]. The introduction of double heterostructure devices [5, 6] commonly used for inorganic laser structures with an emission layer sandwiched between separate charge carrier transport layers allows to significantly increase the luminous efficiency of the devices and to tune the emission wavelength by choosing appropriate dye molecules. Lifetimes exceeding 10000 hours sufficient for practical applications have been demonstrated [7].

2 Organic thin film deposition and device fabrication

For the electroluminescent devices discussed in this paper, transparent ITO-coated glass slides with a sheet resistance of $30\,\Omega/\square$ are cleaned by repeated boiling in organic solvents, mounted onto a 2" sample holder, and introduced into the organic molecular beam deposition (OMBD) system (C. Rompf, p. 47). The reproducible growth process is controlled with a shutter in front of the sample. Following the deposition of the organic layer sequence, metal films are evaporated from tungsten or molybdenum boats. The contact is composed of 200 nm Mg and of 200 nm Ag for protection against atmospheric oxidation. A shadow mask with 2 mm circular holes allows to define the lateral geometry of a simple contact. More advanced structures are obtained by standard photolithography (Hoechst AZ5214 photoresist) and lift-off in acetone.

3 Organic materials

The molecular structures of the organic source materials used for our light emitting diodes are shown in Fig. 1. Preferentially hole transporting behavior is observed for TAD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine) [8] and the triphenylamine-derivative starburst molecule. This novel class of organic compounds yields very homogeneous and stable thin films which are well suited as hole injection layer due to the very low ionization potential of only about 5 eV [9]. PBD (2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3-4-oxadiazole) [10] and $\mathrm{Alq_3}$ (tris-(8-hydroxychinoline) aluminum) serve as electron transport materials. The metal chelate complex $\mathrm{Alq_3}$ is also known for its high fluorescence yield in the green spectral region [11]. Blue emitting electroluminescent devices are fabricated using OXD-8 (1,3-bis(N,N-dimethylaminophenyl)-1,3,4-oxadiazole) as emitter molecule [12]. In addition to organic compounds, rare-earth (RE) complexes, e. g. $\mathrm{Eu(TTFA)_3Phen}$ (europium-tris(1-thenoyl-3-trifluoracetonate)-1,10-phenanthroline), are very promising candidates for light emission in the visible spectral region.

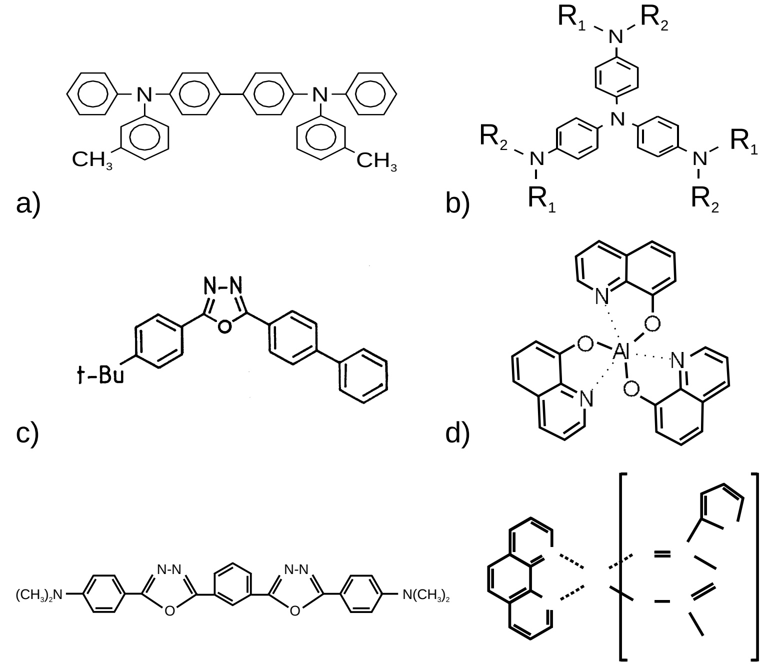

Fig. 1: Molecular structures of (a) TAD, (b) Starburst molecule, (c) PBD, (d) $\mathrm{Alq_3}$, (e) OXD-8, and (f) $\mathrm{Eu(TTFA)_3Phen}$.

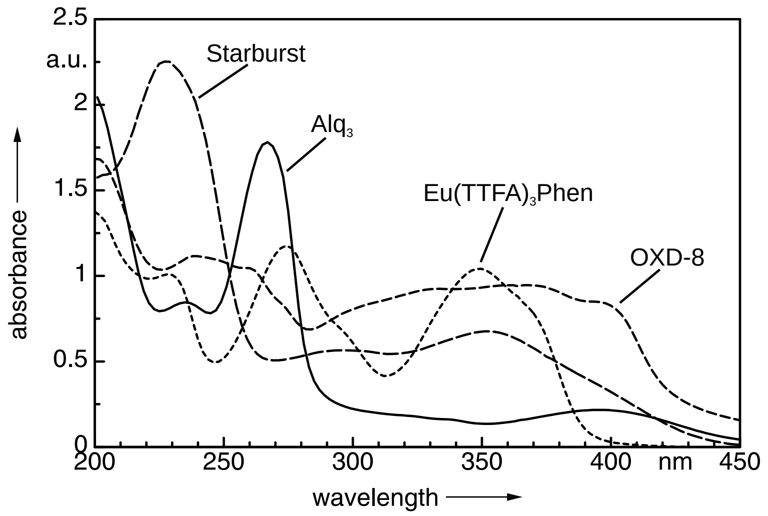

Fig. 2: Absorbance spectra of Starburst molecule, Alq_3, OXD-8, and $Eu(TTFA)_3Phen$.

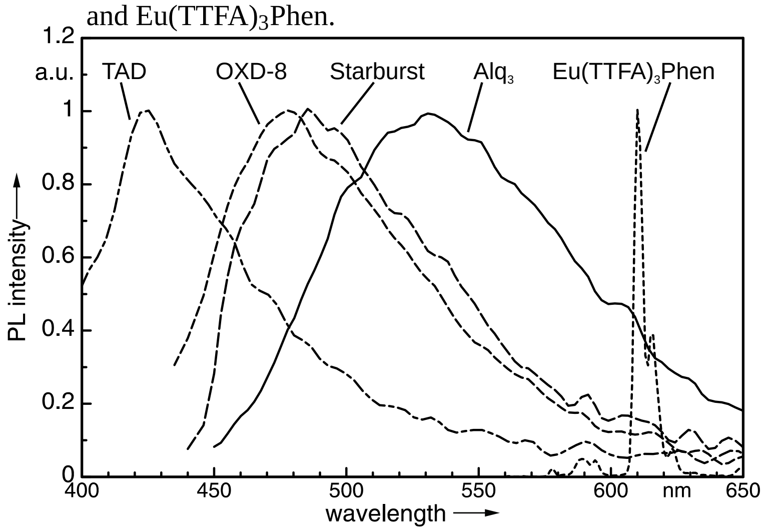

Fig. 3: Normalized photoluminesence spectra of TAD, Starburst molecule, Alq_3, OXD-8, and $Eu(TTFA)_3Phen$.

For optical characterization of the organic compounds, UV-VIS absorbance and photoluminescence spectra were recorded. The absorbance spectra of thin films deposited onto quartz slides are shown in Fig. 2 for the Starburst molecule, Alq_3, OXD-8, and $Eu(TTFA)_3Phen$. The ligand-centered UV absorption bands for the Eu^{3+}- and the Alq_3-complexes are clearly visible. No absorption by the trivalent rare earth ion itself is found due to efficient shielding by the organic ligands.

For photoluminescence measurements, the organic materials were excited with an UV argon ion laser (λ=351 nm, 364 nm). A 200 mm monochromator and a Si photodetector were used to record the spectra shown in Fig. 3. Blue emission was observed for TAD, OXD-8, and the Starburst molecule (λ_{max}=425 nm, 475 nm, 480 nm), Alq_3 showed green emission with a peak wavelength of λ_{max}=530 nm. Fluorescence bandwidths of about 85–90 nm are typical for organic dye molecules. A remarkable Stokes shift of the emission with respect to the lowest absorption bands is found for Alq_3. In contrast to the ligand-centered fluorescence of Alq_3 [13], the emission spectrum of the Eu^{3+}-complex features the characteristic transition lines of the 4f-orbitals of the excited lanthanide ion originating both from the $^5D_1$ and the $^5D_0$ levels to the ^7F levels.

4 Multilayer organic light emitting diodes

4.1 Device structures

The principle of operation of organic light emitting diodes (OLEDs) is similar to that of inorganic light emitting diodes (LEDs). Holes and electrons are injected from opposite contacts into the organic layer sequence and transported to the emitter layer. Recombination leads to the formation of singlet excitons that decay radiatively. In more detail, electroluminescence of organic thin film devices can be divided into five processes [14] that are important for device operation:

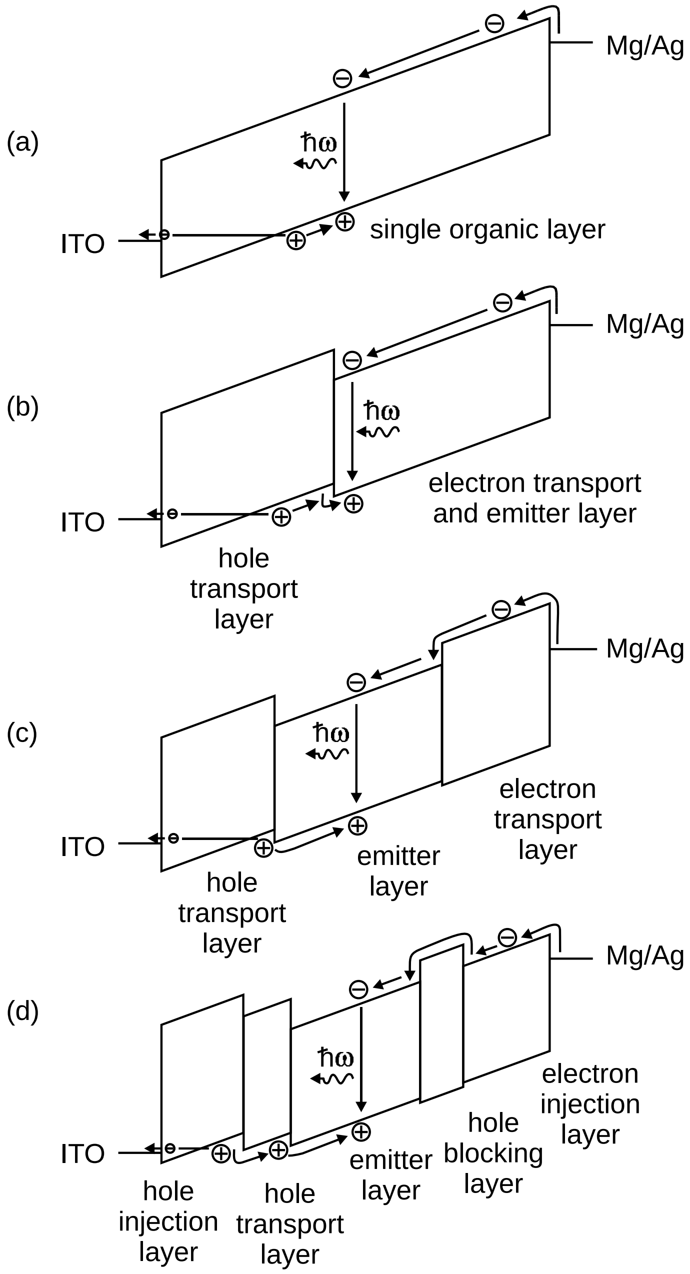

Fig. 4: Layer sequences and energy level diagrams for OLEDs with (a) single layer, (b) single heterostructure, (c) double heterostructure, and (d) multilayer structure with separate hole and electron injection and transport layers.

(a) Injection: Electrons are injected from a low work function metal contact, e. g. Ca or Mg. The latter is usually chosen for reasons of stability. A wide-gap transparent indium-tin-oxide (ITO) or polyaniline (PANI) [15] thin film is used for hole injection. In addition, the efficiency of carrier injection can be improved by choosing organic hole and electron injection layers with a low HOMO (high occupied molecular orbital) or high LUMO (lowest unoccupied molecular orbital) level, respectively.

(b) Transport: In contrast to inorganic semiconductors, high p- or n-conducting organic thin films can only rarely be obtained by doping. Therefore, preferentially hole or electron transporting organic compounds with sufficient mobility have to be used to transport the charge carriers to the recombination site. Since carriers of opposite polarity also migrate to some extent, a minimum thickness is necessary to prevent non-radiative recombination at the opposite contact. Thin electron or hole blocking layers can be inserted to improve the selective carrier transport [16].

(c) Recombination: The efficiency of electron-hole recombination leading to the creation of singlet excitons is mainly influenced by the overlap of electron and hole densities that originate from carrier injection into the emitter layer [17]. Recombination of filled traps and free carriers may also attribute to the formation of excited states [18]. Energy barriers for electrons and holes to both sides of the emitter layer allow to spatially confine and improve the recombination process.

(d) Migration and (e) decay: Singlet excitons will migrate with an average diffusion length of about 20 nm [19] followed by a radiative or non-radiative decay. Embedding the emitter layer into transport layers with higher singlet excitation energies leads to a confinement of the singlet excitons and avoids non-radiative decay paths, e. g. contact quenching. Doping of the emitter layer with organic dye molecules allows to transfer energy from the host to the guest molecule in order to tune the emission wavelength or to increase the luminous efficiency [7].

Efficient device operation not only depends on the choice of molecules with appropriate electronic and optical properties, but also on the design of the device structure. Fig. 4 shows the layer sequences and energy level diagrams of different structures used for our investigations. Electroluminescence is already achieved with a simple single layer device (Fig. 4a), however, the performance is poor since electrons and holes reach the opposite contact and excitons are quenched at the electrodes. The two-layer or single heterostructure device (Fig. 4b) introduces a separate hole transport layer. Holes are injected into the combined emitter and electron transport layer and recombine with electrons near the interface. An optimum thickness is found for the combined layer [20] as a result of sufficient distance of the interface to the metal contact and maximum thickness for a given operating voltage. The double heterostructure (Fig. 4c) well known from laser diodes allows to confine both charge carriers and excitons. Unfortunately, energy barriers at the interfaces still impede the transport of electrons and holes from the contacts to the emitter layer. The complex multilayer structure shown in Fig. 4(d) has separate hole injection and transport layers to form a staircase-like path for holes. A similar layer sequence is used for electron injection. The hole blocking layer prevents holes from penetrating into the electron transport layers whereas the electron injection layer has an intermediate LUMO energy to enhance the electron injection from the Mg contact.

For device characterization, current–voltage and luminance(optical-output-power)–current characteristics are investigated for cw-operation at room temperature and at normal ambient conditions. The luminance was determined with a Minolta LS-110 luminance meter. A large-area Si photodetector (Advantest) was used to measure the optical output power. The electroluminescence spectra were recorded with a 200 mm monochromator or an Anritsu optical spectrum analyzer which also served to provide the chromaticity coordinates.

The internal quantum efficiency of the devices was estimated from the ratio of light generated within the device to light detected by the photodetector. Total reflection at the organic-ITO-glass-air interfaces limits the optical efficiency η_{opt} [21]

$$\eta_{\mathrm{opt}} = 1 - \sqrt{1 - \frac{1}{\bar{n}^2}} \tag{1}$$

to a value of 17 % assuming a refractive index of $\bar{n} = 1.8$ measured for $\mathrm{Alq_3}$. Taking into account Fresnel transmission losses, absorption, and partial reflection at the Mg contact as well as a limited aperture of the photodetector, only about 11-15 % of the light is actually detected, i. e. most of the light is emitted at the edges of the glass slide. Properly designed hemispherical substrates or domes commonly used for inorganic LEDs allow to significantly improve the optical efficiency.

4.2 Green emitting devices

The layer sequences of green emitting devices are depicted in Fig. 5. The single heterostructure OLED consists of a TAD hole transport and an Alq_3 combined emitter and electron transport layer. Additional PBD and Alq_3 thin films are grown as separate hole blocking and electron injection layers for the double heterostructure device. The Alq_3 layer also served as protection for PBD.

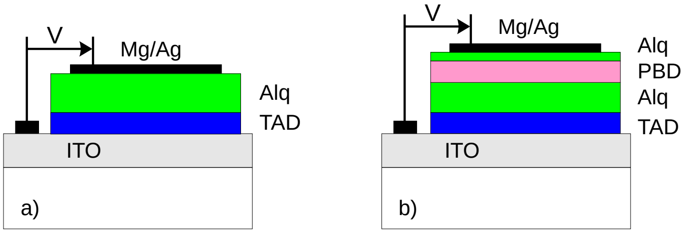

Fig. 5: (a) Single and (b) double heterostructure OLEDs for the green spectral region.

The current–voltage and luminance–current characteristics of the green single heterostructure (30 nm TAD, 50 nm Alq_3) and double heterostructure (30 nm TAD, 50 nm Alq_3, 20 nm PBD, 10 nm Alq_3) are shown in Fig. 6. The turn-on voltages of 9 V and 12 V, respectively, are mainly determined by the total layer thickness of the devices. However, the insertion of a electron transport (i. e. hole blocking) layer prevents injected charge carriers and excitons from reaching the opposite contact followed by non-radiative recombination and decay. The estimated internal quantum efficiency increases from 4.7 % to 8.5 % (at 5 mA) whereas luminous efficiencies of 1.0 lm/W and 1.4 lm/W, respectively, are obtained.

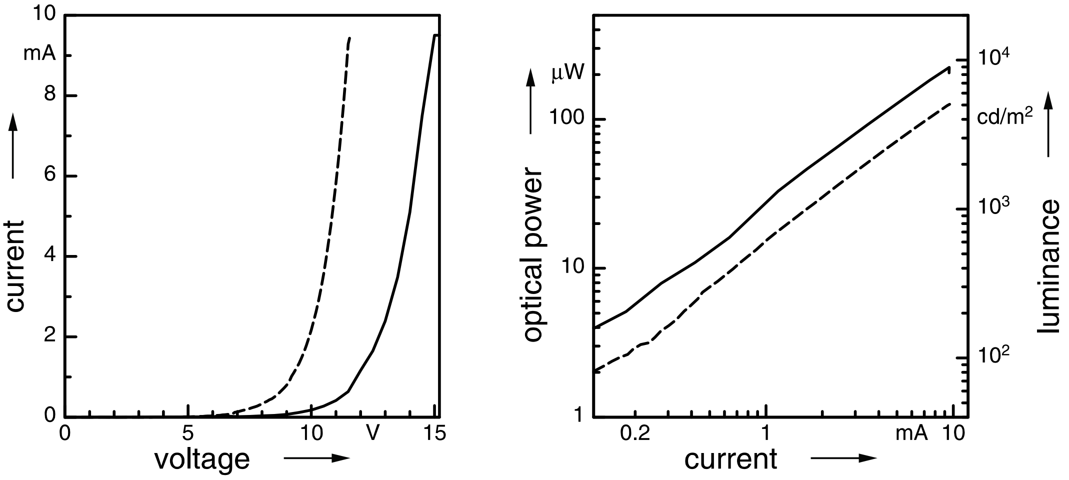

Fig. 6: Current–voltage and luminance–current characteristics of the green emitting devices: single heterostructure (- -) and double heterostructure (—).

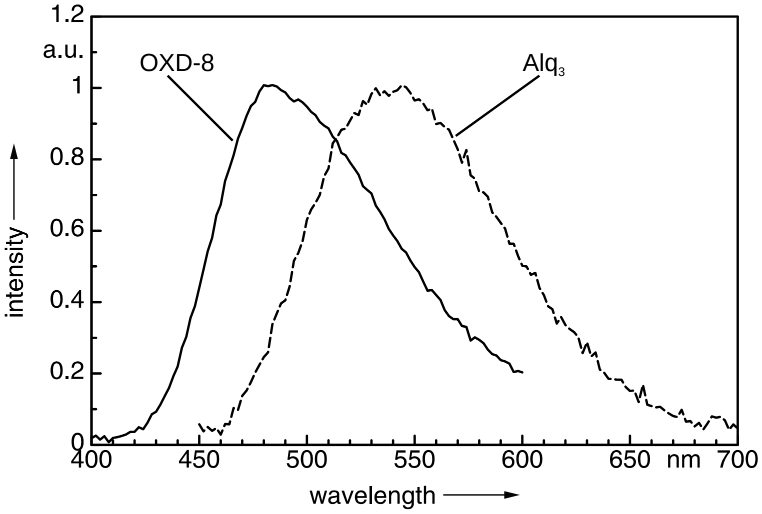

Fig. 7: Electroluminescence spectra of the green (- - -) and blue (—) OLEDs.

Fig. 7 shows the electroluminescence spectrum of the green emitting diodes with a peak wavelength of 535 nm and a half width of 105 nm. Good agreement with the photoluminescence spectrum of Alq_3 (Fig. 3) is observed.

4.3 Blue emitting devices

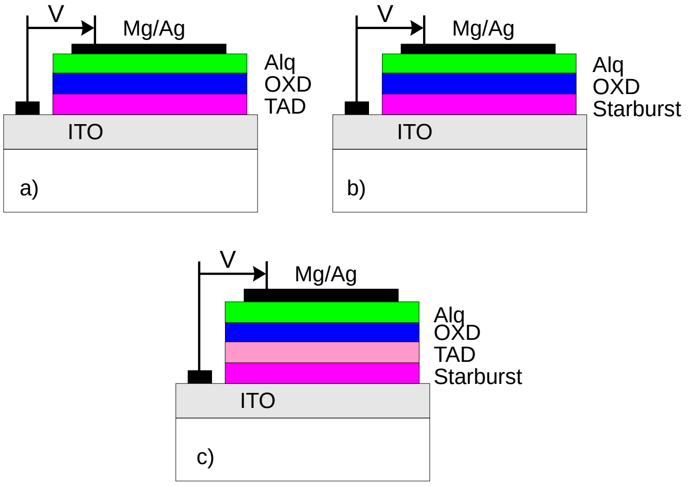

Fig. 8: Multilayer OLEDs for the blue spectral region with different hole transport layer sequences (a) - (c).

Three different double heterostructure blue emitting diodes were fabricated to investigate the effect of an additional hole injection layer. Fig. 8 shows the structures of devices with a single hole transport layer (TAD and Starburst, Fig. 8(a) and (b), respectively) and with separate hole injection and transport layers (Starburst and TAD, Fig. 8(c)). Alq_3 is used as electron transport material.
Blue emission with a peak wavelength of 480 nm and a half width of 95 nm was observed. The good agreement of the emission characteristics with the photoluminescence spectrum (Fig. 3) indicates that OXD-8 is responsible for the electroluminescence.

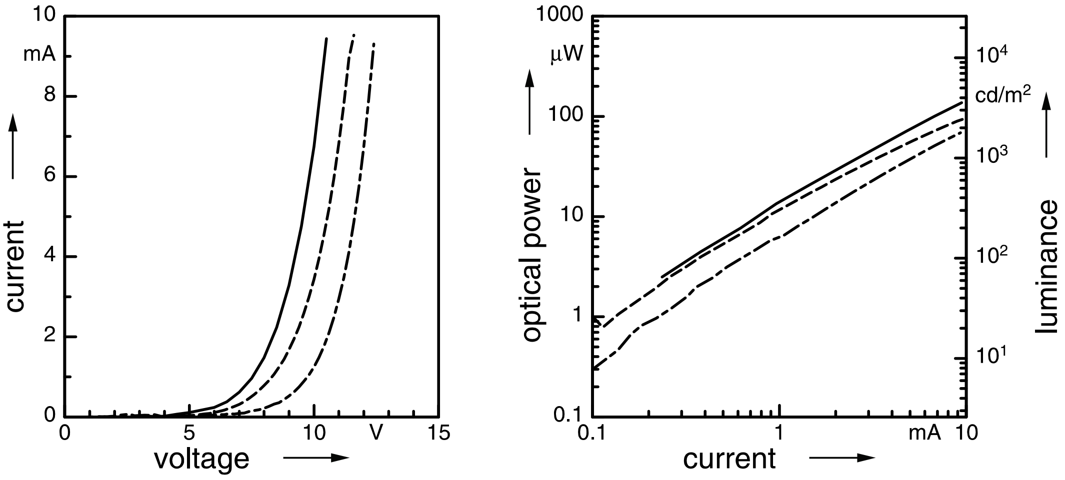

Fig. 9: Current–voltage and luminance–current characteristics of the blue emitting device with different hole transport layers: Starburst/TAD (—), Starburst (- - -), and TAD (- · -).

The current–voltage and luminance–current characteristics of OLEDs with 20 nm hole transport layer (15 nm Starburst and 5 nm TAD, respectively), 30 nm OXD-8, and 20 nm Alq_3 are shown in Fig. 9. The turn-on voltage, the internal quantum efficiency, and the luminous efficiency are already improved for an OLED with the Starburst molecule as hole transport material (8 V, 0.5 lm/W, 3.3 %) compared to the standard TAD device (10 V, 0.3 lm/W, 2.2 %). The combination of Starburst hole injection and TAD transport layers allows both to achieve turn-on voltages below 7 V and to increase the internal quantum (luminous) efficiency to 4.3 % (0.8 lm/W).

The energy level diagram (Fig. 4) allows to explain this result. Holes injected into the TAD layer are efficiently transported to the emitter layer, however, the injection process from the ITO electrode into TAD is limited by the large energy barrier. In contrast, holes can easily be injected into the Starburst layer. The insertion of an additional TAD thin film between the Starburst and the emitter layers reduces the energy barrier that is encountered at the Starburst/OXD-8 interface. The staircase-like HOMO level sequence provides a better hole injection and transport path and improves the overall device performance.

4.4 OLEDs for Flat Panel Displays

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 [22], 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.

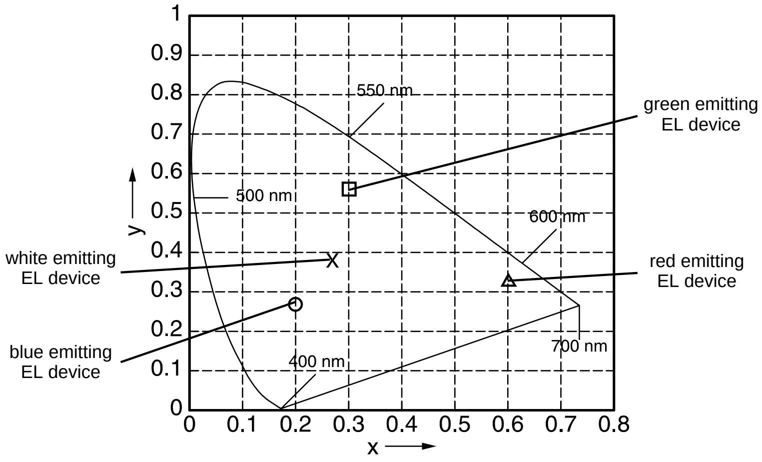

Fig. 10: Chromaticity diagram with CIE coordinates of the blue, green, red, and white emitting electroluminescent devices.

The color perception of the blue, green (and red) emitting OLEDs is summarized in the chromaticity diagram shown in Fig. 10. The emission color can be varied over the entire visible spectral region by choosing appropriate dye molecules. Guest-host systems, i. e. doped organic thin films, have also been intensively studied [19, 23].

White light emitting OLEDs are obtained by combining different fluorescent dye molecular layers [24, 25]. The thickness of the Alq_3 and OXD-8 layers of the double heterostructure devices (Fig. 8) can be adjusted to achieve bluish-green/white emission originating equally from the two molecules. The CIE coordinate of the white OLED is also shown in Fig. 10. An additional emitter, e. g. a DCM (4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran) doped Alq_3 thin film or a Eu^{3+}-complex layer, provides the red component.

5 Conclusions

Multilayer structures with properly chosen organic transport materials and emitter dyes are a successful approach for the fabrication of light emitting diodes for the visible spectral region.

The organic molecular beam deposition (OMBD) under vacuum conditions offers precise layer thickness control and substrate cooling crucial for the growth of homogeneous and smooth organic thin film. With respect to the operation and performance of OLEDs, double heterostructure devices allow to efficiently inject and transport electrons and holes to the emitter layer and to spatially confine the recombination process. In addition, migration and decay of singlet excitons are also restricted resulting in drastically improved luminous and quantum efficiencies compared to simple single layer devices. Green emitting OLEDs based on Alq_3 showed maximum values of 1.4 lm/W and 8.5 %, respectively.

Further device optimization was achieved with a multilayer structure consisting of a separate hole injection layer inserted between the ITO-contact and the hole transport layer. Thin films of the triphenylamine derivative Starburst molecule in combination with TAD used for a blue emitting OXD-8 based OLEDs allow to decrease the hole transport layer thickness and to obtain both lower turn-on voltages of only about 7 V and higher luminous and internal quantum efficiencies of 0.8 lm/W and 4.3 %, respectively.

References

[1] C. W. Tang, S. A. VanSlyke: *Organic electroluminescent diodes*, Appl. Phys. Lett., **51**, 913–915, 1987

[2] S. Saito, T. Tsutsui, M. Era, N. Takada, C. Adachi, T. W. Y. Hamada: *Progress in organic multilayer electroluminescent devices*, Proc. SPIE, **1910**, 212–221, 1993

[3] D. R. Baigent, N. C. Greenham, J. Grüner, R. N. Marks, R. H. Friend, S. C. Moratti, A. B. Holmes: *Light-emitting diodes fabricated with conjugated polymers - recent progress*, Synth. Met., **67**, 3–10, 1994

[4] S. R. Forrest, P. E. Burrows, E. I. Haskal, F. F. So: *Ultrahigh-vacuum quasiepitaxial growth of model van der Waals thin films. II. Experiment*, Phys. Rev. B, **49**, 11309–11321, 1994

[5] C. Adachi, S. Tokito, T. Tsutsui, S. Saito: *Electroluminescence in organic films with three-layer structure*, Jpn. J. Appl. Phys., **27**, L269–L271, 1988

[6] C. Adachi, T. Tsutsui, S. Saito: *Confinement of charge carriers and molecular excitons within 5-nm-thick emitter layer in organic electroluminescent devices with a double heterostructure*, Appl. Phys. Lett., **57**, 531–533, 1990

[7] Y. Hamada, T. Sano, K. Shibata, K. Kuroki: *Influence of the emission site on the running durability of organic electroluminescent devices*, Jpn. J. Appl. Phys., **34**, L824–L826, 1995

[8] M. Stolka, J. F. Yanus, D. M. Pai: *Hole transport in solid solutions of a diamine in polycarbonate*, J. Phys. Chem., **88**, 4707–4714, 1984

[9] Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, K. Imai: *Multilayered organic electroluminescent device using a novel starburst molecule, 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine and as a hole transport material*, Appl. Phys. Lett., **56**, 807–809, 1994

[10] C. Adachi, T. Tsutsui, S. Saito: *Organic electroluminescent device having a hole conductor as an emitting layer*, Appl. Phys. Lett., **55**, 1489–1491, 1989

[11] Y. Hamada, T. Sano, M. Fujita, Y. Nishio, K. Shibata: *Organic electroluminescent devices with 8-hydroxyquinoline derivative-metal complexes as an emitter*, Jpn. J. Appl. Phys., **32**, L514–L515, 1993

[12] Y. Hamada, C. Adachi, T. Tsutsui, S. Saito: *Blue-light-emitting organic electroluminescent devices with oxadiazole dimer dyes as an emitter*, Jpn. J. Appl. Phys., **31**, 1812–1816, 1992

[13] R. Ballardini, G. Varani, M. T. Indelli, F. Scandola: *Phosphorescent 8-quinolinol metal chelates. Excited-state properties and redox behavior*, Inorg. Chem., **25**, 3858–3865, 1986

[14] E. Aminaka, T. Tsutsui, S. Saito: *Electroluminescent behaviors in multilyer thin-film electroluminescent devices using 9,10-bisstyrylanthracene derivatives*, Jpn. J. Appl. Phys., **33**, 1061–1068, 1994

[15] Y. Yang, E. Westerweele, C. Zhang, P. Smith, A. J. Heeger: *Enhanced performance of polymer light-emitting diodes using high-surface area polyaniline network electrodes*, J. Appl. Phys., **77**, 694–698, 1995

[16] J. Kido, M. Kimura, K. Nagai: *Multilayer white light-emitting organic electroluminescent device*, Science, **267**, 1332–1334, 1995

[17] K. C. Kao, W. Hwang: Electrical transport in solids, Pergamon Press, Oxford, 1981

[18] S. R. Forrest, P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, M. E. Thompson: *Current conduction and electroluminescence mechanisms in molecular organic light emitting devices*, Proc. OSA/ACS Topical Meeting on Organic Thin Film for Photonics Applications, 217–220, Portland, OR, USA, 1995

[19] C. W. Tang, S. A. VanSlyke, C. H. Chen: *Electroluminescence of doped organic thin films*, J. Appl. Phys., **65**, 3610–3616, 1989

[20] D. Ammermann, A. Böhler, C. Rompf, W. Kowalsky: *Characterization and optimization of high brightness organic light emitting diodes (OLEDs)*, Proc. IEEE/LEOS Summer Topical Meeting on Flat Panel Display Technology, 31–32, Keystone, CO, USA, 1995

[21] S. M. Sze: Physics of semiconductor devices, Wiley & Sons, Inc., New York, 1981

[22] R. L. Moon: *Organic EL devices for displays*, IS&T's 48th Annual Conference Proceedings, 386–391, 1995

[23] T. Mori, K. Miyachi, T. Kichimi, T. Mizutani: *Electrical and luminescent properties of color-changeable organic electroluminescent diode using squarylium dyes*, Jpn. J. Appl. Phys., **33**, 6594–6598, 1994

[24] J. Kido, K. Hongawa, K. Okuyama, K. Nagai: *White light-emitting organic electroluminescent devices using the poly(N-vinylcarbazole) emitter layer doped with three fluorescent dyes*, Appl. Phys. Lett., **64**, 815–817, 1994

[25] M. Strukelj, R. H. Jordan, A. Dodabalapur: *Organic multilayer white light emitting diodes*, J. Am. Chem. Soc., **118**, 1213–1214, 1996