Device Structures and Materials for Organic Light Emitting Diodes

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Organic light emitting devices (OLEDs) are promising candidates for light-weight color flat panel displays. Different device structures with emission in the blue, green, and red spectral region are discussed with respect to their optical and electrical characteristics. Blue OLEDs based on OXD-8 as emitter molecule show quantum efficiencies of 0.9% (2.2 cd/A, 0.6 lm/W), green emitting devices based on Alq3 achieve values of 1.4% (4.9 cd/A, 1.3 lm/W). Electroluminescence with colors tunable from yellow-green to red is obtained with DCM doped Alq3 layers. To investigate the device physics, a thin DCM:Alq3 sensor film is inserted into an Alq3 emitter layer. Position and current dependent spectral characteristics allow to explain the device behavior. Carrier injection, transport, recombination, exciton diffusion and decay are identified as the crucial processes responsible for the operation of OLEDs.

1. Introduction

A new class of materials for light-weight color flat panel displays 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. 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. The introduction of single and double heterostructure devices 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 [2].

In this paper, we describe the growth of organic thin films by the organic molecular beam deposition (OMBD) technique. Molecules suitable for electron and hole transport as well as fluorescent dyes for the visible spectral region are presented. The performance of multilayer devices is discussed with respect to layer sequence and thickness in terms of their electrical behavior and quantum efficiencies. A doping technique is used to investigate carrier recombination and exciton diffusion processes. The analysis of the current-voltage characteristics and simulation results allow to identify the dominant carrier injection and transport mechanisms.
2. Organic Source Materials and Molecular Beam Deposition

The molecular structures of the organic source materials used for 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 and the starburst type molecule TNATA (4,4’,4”-tris(N-(1-naphthyl)-N-phenyl-amino)-triphenylamine. This novel class of organic compounds yields very homogeneous and stable thin films which are well suited as hole injection layer due to the low ionization potential of only about 5 eV [3]. PBD (2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3-4-oxadiazole) and Alq3 (tris-(8-hydroxyquinoline) aluminum) serve as electron transport materials. The metal chelate complex Alq3 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]. DCM (4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran) doped into Alq3 layers shows concentration dependent emission in the yellow and red spectral region [5].

The organic source materials are sublimated under ultrahigh vacuum conditions from effusion cells. The sublimation temperatures are controlled within 0.1°C for reproducible growth conditions and vary from 100 to 450°C depending on the organic material. Low growth rates of 2 – 8 nm/min yield smooth and homogeneous thin films. A quartz oscillator allows to monitor the layer thickness on a nanometer scale. For the electroluminescent devices discussed in this paper, transparent ITO-coated glass slides with a sheet resistance of 30 Ω/□ are cleaned by repeated boiling in organic solvents, mounted onto a 2” sample holder, and introduced into the organic molecular beam deposition OMBD system. 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.

3. Device Structures and Characterization

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 [6] that are important for device operation:

(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) 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.

(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. Recombination of filled traps and free carriers may also attribute to the formation of excited states. Energy barriers for electrons and holes to both sides of the emitter layer allow to spatially confine and improve the recombination process.

(d) Exciton diffusion and (e) decay: Singlet excitons will migrate with an average diffusion length of about 20 nm 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. quenching at the contacts. 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.

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. 2 shows the layer sequences and energy level diagrams of different structures. Electroluminescence is already achieved with a simple single layer device (Fig. 2a), 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. 2b) introduces a separate hole transport layer. Holes are injected into the common emitter and electron transport layer and recombine with electrons near the interface. An optimum thickness is found for the combined layer [7] 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. 2c) 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. 2(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 DC device characterization, current–voltage and luminance (optical–output–power)–current characteristics are investigated at room temperature and 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 and a Si photodetector. Fig. 3 shows the calibrated spectra of the green and blue emitting diodes with peak wavelengths (half widths) of 535 nm (105 nm), and 480 nm (95 nm), respectively. In addition, the dopant dependent spectra of OLEDs with DCM:Alq₃ emitter layers are shown for DCM concentrations of 0.2 %, 1 %, and 5 %. The peak wavelength is shifted from 535 nm for the undoped structure to 565 nm, 590 nm, and 620 nm for the DCM doped devices.
3.1 Green Emitting Devices

The layer sequences of green emitting devices are depicted in Fig. 4. The single heterostructure OLED consists of a TAD hole transport and an Alq$_3$ 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 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. 5. The operation voltages at 30 mA/cm$^2$ of 9.2 V and 11.8 V are mainly determined by the total layer thickness of the devices. However, the insertion of an electron transport (i.e. hole blocking) layer prevents injected charge carriers and excitons from reaching the opposite contact. The external quantum efficiency increases from 0.66% to 1.4% whereas luminous efficiencies of 0.8 lm/W and 1.3 lm/W, respectively, are obtained.

3.2 Blue Emitting Devices

Three different double heterostructure blue emitting diodes were fabricated to investigate the effect of an additional hole injection layer. Fig. 6 shows the structures of devices with a single hole transport layer (TAD and TNATA, Fig. 6(a) and (b), respectively) and with separate hole injection and transport layers (TNATA and TAD, Fig. 6(c)). Alq$_3$ is used as electron transport material. In addition, a device with a combination of PBD and Alq$_3$ electron transport layers is shown in Fig. 6(d).
The current–voltage and luminance–current characteristics of OLEDs with 20 nm hole transport layer (15 nm TNATA and 5 nm TAD, respectively), 30 nm OXD-8, and 20 nm Alq₃ are shown in Fig. 7. The four layer device (d) has a slightly different optimum layer sequence with 30 nm TAD, 100 nm OXD-8, 20 nm PBD, and 10 nm Alq₃.

The operation voltages, the external quantum efficiency, and the luminous efficiency are already...
improved for an OLED with the starburst molecule as hole transport material (8.1 V, 0.56 %, 0.51 lm/W) compared to the standard TAD device (9.5 V, 0.35 %, 0.28 lm/W). The combination of TNATA hole injection and TAD transport layers allows both to achieve an operation voltage of only 7.3 V and to increase the external quantum efficiency to 0.71 % (0.72 lm/W). The total layer thickness of 160 nm for device (d) leads to an increased voltage of 12.6 V at 30 mA/cm², but improves the quantum efficiency to 0.94 % (0.55 lm/W).

The energy level diagram (Fig. 2) allows to explain these results. 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 TNATA layer. The insertion of an additional TAD thin film between the TNATA and the emitter layers reduces the energy barrier that is encountered at the TNATA/OXD-8 interface. The staircase-like HOMO level sequence provides a better hole injection and transport path and improves the overall device performance. The PBD film in device (d) has a larger singlet energy than OXD-8 and avoids exciton diffusion processes into the Alq₃ electron injection layer.

### 3.3 Red Emitting Devices

The layer sequence of the yellow and red OLEDs with 30 nm TAD hole transport, 30 nm DCM:Alq₃ emitter, and 20 nm Alq₃ electron transport layer are shown in Fig. 8. The device structure and the electrical characteristics are similar to the single heterostructure green emitting diode (Fig. 4(a)). However, the doping introduces additional traps leading to an increase in operation voltage as shown in Fig. 9. The quantum efficiency has a maximum for a dopant concentration of about 1 % and drops beyond 5 % due to bimolecular exciton quenching.

The efficiency of OLEDs with doped emitter layers depends on a large overlap of the emission spectrum of the host material and the absorption spectrum of the dopant. In DCM:Alq₃ devices,
electrons are trapped in Alq₃ host molecules [8] and recombine with holes injected into the emitter layer to create Alq₃ excitons. The singlet excitons efficiently transfer their energy to DCM:Alq₃ emission complexes in a Förster type process. The excited DCM:Alq₃ complexes have a lower singlet state energy and decay radiatively determined by the fluorescence yield. In addition, DCM molecules can trap holes injected into the emitter layer and serve as recombination center.

4. Doping Technique

A thin doped film inserted into the layer sequence allows to investigate carrier recombination and exciton diffusion processes. This doping technique [9] is based on an efficient energy transfer to dopant-host complexes formed within the sensor layer. Excitons migrating into the doped thin film transfer their energy and lead to emission shifted to the red spectral region. The ratio of emitter material and dopant emission provides information about the recombination site and exciton diffusion length.
The simple TAD/Alq₃ single heterostructure is modified by inserting a 5 nm thin DCM:Alq₃ layer with a distance of 0 nm, 15 nm, and 30 nm from the interface (Fig. 10(a)). Excitons generated between the DCM:Alq₃ sensor layer and the TAD/Alq₃ migrate in both directions with an average exciton diffusion length \( L_{\text{ex}} \). Migration into the sensor layer leads to an efficient energy transfer and the excitation of DCM:Alq₃ states. Assuming one-dimensional exciton diffusion, the stationary exciton density is given by

\[
n_{\text{ex}}(x) \propto \exp\left(-\frac{x}{L_{\text{ex}}}\right).
\]  

Integrating (1) yields the number of excitons per unit area \( N(x_d) \) that decay within the Alq₃ layer as a function of recombination site \( x_r \) and position of doping layer \( x_d \):

\[
N(x_d) = N_0 \left[ 1 - \frac{1}{2} \exp\left(-\frac{x_d - x_r}{L_{\text{ex}}}\right) - \frac{1}{2} \exp\left(-\frac{x_d + x_r}{L_{\text{ex}}}\right) \right].
\]  

In this simple model, the recombination zone is considered to be localized at \( x_r \). An estimate of its actual width of about 3 – 6 nm is found for a Langevin recombination model \[10\]. Excitons are assumed to be reflected at the TAD/Alq₃ interface.

Fig. 10(b)-(d) show the electroluminescence spectra recorded for low, medium, and high current densities. The dopant concentration was 4 % leading to a peak wavelength of the DCM:Alq₃ layer of 610 nm. The spectra for devices with sensor layer distances of 15 nm and 30 nm indicate an increase in Alq₃ emission with increasing current density due to a shift of the recombination zone towards the interface. An analysis of the emission ratio using (2) leads to the current dependence of the recombination site shown in Fig. 11 determined by the overlap of positive and negative space charge regions due to the low mobility of charge carriers and traps. The recombination zone is located within the emission layer for low current densities and reaches the interface at about 10 mA/cm². Higher injection levels lead to an accumulation of electrons at the TAD/Alq₃ barrier in the LUMO level. The calculated diffusion length of 20 nm is current independent.

The emission behavior shown in Fig. 10(b) for a device with a sensor layer located directly at the interface differs significantly. At low injection levels, the recombination is located within the DCM:Alq₃ layer since only a small portion of emission from the Alq₃ layer is observed. Additional traps introduced by the DCM molecules lead to a redistribution of space charge regions and
to recombination at the interface. At higher current densities, holes may reach the Alq$_3$ layer, recombine with electrons, and generate Alq$_3$ excitons. The width of the recombination zone is therefore approximately equal to the sensor layer thickness.

5. Current Injection and Transport

The doping technique provides information about the recombination and exciton diffusion processes with an organic light emitting diode. The electrical characteristics, however, are determined by injection and transport processes. A number of different models have been put forward to explain the device behavior. The current-voltage characteristics of the TAD/Alq$_3$ green OLED are plotted in Fig. 12 according to the relations describing injection and transport mechanisms: (a) \(\log J - \log V\) for space charge and trap limited transport \([11]\), (b) \(\log J/F^{3/4} - F^{1/2}\) for thermionic emission \([12]\), (c) Fowler-Nordheim plot \(\log J/F^2 - 1/F\) for tunnel injection \([13]\), and (d) \(\log J - 1/F^{1/2}\) for ballistic injection \([14]\).

Assuming an electron mobility of \(5 \cdot 10^{-5} \text{ cm}^2/\text{V}s\) in the Alq$_3$ layer and an effective thickness of 60 nm to take into account the voltage drop across the TAD layer, a trap density of \(3 \cdot 10^{18} \text{ cm}^{-3}\) for an exponential trap distribution with an energy \(E_t = 0.16 \text{ eV}\) is calculated. Below a turn-on voltage of 2.4 V, the slope of the I-V characteristics is only 1.7 indicating space charge limited transport. Since the energy of the electron-hole pair is below the singlet energy of an Alq$_3$ exciton (2.8 eV), bulk recombination may not take place and lead to predominantly hole current transport. The onset of electroluminescence observed at this voltage supports the argument. The energy difference of 0.4 eV is probably provided by thermionic emission over the Mg/Alq$_3$ barrier. Since different contact metals have a strong influence on the operation voltages, injection mechanisms cannot be neglected.

However, plot (b) yields only a barrier of 0.3 eV for thermionic emission which is significantly lower than the value of 0.6 eV found from the difference in work function of Mg and LUMO level of Alq$_3$. In addition, at this barrier height, tunnel injection dominates current injection for electric fields larger than about 0.5 MV/cm, yet, the Fowler-Nordheim plot does not show a good agreement. The mean scattering length obtained for the ballistic injection model in (d) of only 0.06 nm is also not adequate.

Time-of-flight measurements show that the electron and hole mobilities are strongly field and temperature dependent \([15]\). The Poole-Frenkel model provides a satisfactory fit to these results. However, the characteristic due to field dependent mobility alone does not agree with the device behavior shown in Fig. 12.

To simulate the current-voltage characteristics, we consider trap-limited current transport \([8]\), a Poole-Frenkel model for carrier mobility \([15, 16]\), and tunnel injection at the contacts \([12]\). We employ a regional approximation model \([17]\) for the calculation, dividing the Alq$_3$ layer into three regions (Fig. 13) in which only the dominating processes are taken into account.

In region I, next to the electron-injecting contact, trap-limited electron conduction is assumed, whereas holes are the majority carriers in region III, where traps can thus be neglected. Current density and Poisson equation for regions I and III are
Fig. 12: Current-voltage characteristics for different injection and transport mechanisms: (a) \( \log J - \log V \) for space charge and trap limited transport, (b) \( \log J/F^{3/4} - F^{1/2} \) for thermionic emission, (c) Fowler-Nordheim plot \( \log J/F^2 - 1/F \) for tunnel injection, and (d) \( \log J - 1/F^{1/2} \) for ballistic injection.

The intrinsic carrier density is \( n_0 = 10^{11} \text{ cm}^{-3} \), and \( n_t \) is the number of occupied traps for an exponential trap distribution. The electron mobility is given by a Poole-Frenkel model

\[
\mu_n = \mu_{n0} \exp \left( - \frac{E_a - \beta_p F^2}{k T_{\text{eff}}} \right)
\]
Fig. 13: Regional approximation model for the simulation of a single-layer device.

Fig. 14: Calculated electron and hole densities, and electric field in a single-layer structure.

with \( \beta_{PF} = (q^3/\pi \varepsilon)^{1/2} \), \( T_{eff} = T^{-1} - T_0^{-1} \), \( \mu_{n0} = 1.5 \cdot 10^{-2} \text{ cm}^2/\text{Vs} \), \( T_0 = 570 \text{ K} \), \( E_a = 0.73 \text{ eV} \). The hole mobility is assumed proportional to the electron mobility \( \mu_p = 0.01 \mu_n \).

In region II, recombination of electrons and holes takes place. The Poisson equation is

\[
\frac{dF}{dx} = \frac{q}{\varepsilon} (n_0 - n - n_t + p)
\]

and with drift-diffusion and continuity equations, recombination is taken into account by

\[
R = q \frac{dF}{dx} (\mu_n nF) = q \frac{dF}{dx} (\mu_p pF)
\]

\( R \) is calculated from a modified Shockley-Read-Hall model [8, 18], assuming traps with an exponential trap density as recombination centers.

The system of differential equations is solved employing a shooting method. The current density \( J \) is given and \( F(0), F(d) \) are calculated from a Fowler-Nordheim equation for \( J \). Barrier heights are 0.3 eV and 0.4 eV for injection of holes and electrons, respectively. With these initial values and \( x_1 \), equations for regions I and III are integrated using a step-adaptive 4th-order Runge-Kutta method. Boundary conditions at the region interfaces are continuity of potential, electric field, and carrier densities. At \( x_1 \), an arbitrary, very small minority carrier density is assumed. Results are independent of the exact number. Integrating region II, \( x_2 \) is determined from \( \eta \mu_n \leq 10^{-5} p \mu_p \). \( x_1 \) is iterated until electric fields at \( x_2 \) in regions II and III match.

A typical result is shown in Fig. 14. The recombination zone is located within the Alq3 layer, its width is on the order of 2 - 6 nm. Fig. 15 shows a comparison of current-voltage characteristics and
the location of the recombination zone for calculations including no traps and constant mobility (— — —), exponential trap distribution and constant mobility (— — —), no traps and Poole-Frenkel model (— — —), exponential trap distribution and Poole-Frenkel model (——).

The last model is the only one to grow with a power law \((m = 7 \ldots 8)\) in a current range of several orders of magnitude. The recombination zone generally shifts correctly, but it is located far closer to the electron-injecting contact than determined from our experiments. This may be due to an insufficient contact model, since the current-voltage curve does not change its slope correctly below approximately 2.8 V, either. At low voltages, thermionic or ballistic injection may be dominating, which has not been included, here. Generally, the calculated device characteristics at low injection levels are strongly dependent on the contact model. Carrier accumulation processes at the heterobarrier have not been considered, either. Finally, the temperature dependence of the I-V characteristics is modeled satisfactorily.

6. Conclusions

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

Blue, green, and red emitting OLEDs fabricated by organic molecular beam deposition (OMBD) achieve external quantum efficiencies of 1–1.5 % with OXD-8, Alq3, and DCM:Alq3 emission layers. Guest-host systems provide a means to tune the emission wavelength and to increase the efficiency. In addition, thin doped sensor layers inserted into the device allow to obtain information about recombination and exciton diffusion processes. An analysis of the electrical characteristics

Fig. 15: Calculated recombination site and current-voltage characteristics of Alq3 single layer devices: (——) trap-free, constant mobility, (- - -) traps, constant mobility, (— —) trap-free, Poole-Frenkel model, and (— — —) traps, Poole-Frenkel model.
and a numerical simulation show that different injection and transport mechanisms determine the spatial extent of space charge regions and the location of the recombination zone.

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