

Organic White Light-Emitting Diodes based on Luminescence Down-Conversion

Deutsche Übersetzung des Titels:

**Erzeugung von weißem Licht durch die Konversion der
Lumineszenz von organischen Leuchtdioden**

Der Technischen Fakultät der
Universität Erlangen-Nürnberg
zur Erlangung des Grades

D O K T O R – I N G E N I E U R

vorgelegt von

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Als Dissertation genehmigt von
der Technischen Fakultät der
Universität Erlangen-Nürnberg

Tag der Einreichung:	26.11.2007
Tag der Promotion:	02.06.2008
Dekan:	Professor Dr. J. Huber
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*To Fritz Arthur Uhlmann (*1906-†1992)*

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1. Introduction

1.1. Motivation

Clearly, lighting has played a major role in human life since a piece of burning wood was “invented” 500,000 years ago. Torches, later candles and oil lamps, separated lighting from heating. Gas lighting (1772), electric lighting (1876) and fluorescent lamps (1938) were milestones in lighting technology.

Contemplating the total primary energy consumption, today lighting accounts for about 20 % of all the electricity produced [Misr06], which brings out the relevance of lighting in daily life. Furthermore, this number underlines the importance of developing highly efficient light sources, considering increasing environmental problems due to the growing global energy consumption. Since the invention of the inorganic red light emitting diode (LED) in 1962 [Holo62], solid state lighting has been developed to a technology which allows replacing incandescent and fluorescent lamps by more efficient and more durable devices. It is estimated that by 2025 solid state lighting could reduce the global amount of electricity used for lighting by 50%; no other electricity consumer has such a large energy-savings potential [DOE01]. Now a new competitor for inorganic LEDs is coming onto the market that is based on organic semiconductors.

Initial point of the development of organic light emitting diodes (OLEDs) was research work published by C.W. Tang and S.A. Vanslyke in 1987 [Tang87]. Electroluminescence from thin layers of organic molecules processed by evaporation was reported in this publication. The results demonstrated the capacity of OLEDs for the first time. Three years later Burroughes *et al.* showed that light-emitting devices can also be fabricated based on polymers [Burr90]. Today numerous academic and industrial research teams are focusing on both technologies, i.e. solution processable polymer OLEDs and small molecule OLEDs fabricated by an evaporation process. The first commercial OLED product was available in 1997, when Pioneer brought the first display based on small molecules onto the market. The first commercial application of a polymer OLED was the display of an electric shaver by Phillips in 2002 [Phil03].

Now OLED technology is on the verge of creating commercial applications in the lighting sector. The remarkable advantages of OLEDs will drive innovative products and open new fields of application: They are thin, flat and lightweight. The thickness of the diode itself comprising the electrodes and the organic layers sandwiched in between is below 1 μm . However, the thickness of the device is basically determined by the substrate and the encapsulation; at the state of the art the thickness of the resulting device can be reduced below 1 mm. Furthermore, the technology offers the production of large area lighting panels in a cheap and simple process.

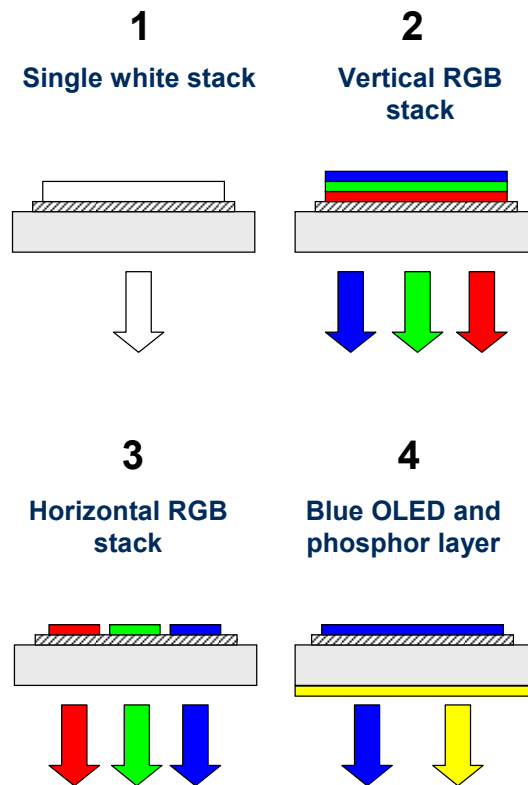


Fig. 1-1. Schemes of the four general approaches to generate white light based on organic light-emitting devices.

White light-emitting OLEDs can be generated by four approaches, schematically shown in Fig. 1-1: (1) A single white emitting stack, where the white emission is achieved by using a combination of different emissive components providing red, green, and blue light from a single emitting layer [Slyk00]. This device architecture offers easy processing but it is not easy to tune the color without affecting device performance. (2) A vertical red-green-blue (RGB) stack where the output spectrum of such a device is determined by the three light-

emitting components [Shen01]. This device architecture leads to color homogeneity over the active area but relies on complex processing methods. (3) A horizontal RGB stack where the output spectrum of a horizontal stack can be changed while operating the device when addressing the patterns separately. Current methods to manufacture a device in this way rely on expensive printing techniques. For all the above mentioned methods, color stability is difficult to be achieved due to different lifetime aging rates of the emitters involved. Method (4) is using a single blue emitting OLED in combination with a down-conversion layer. Here a luminescence converting material (phosphor) coated on the underlying OLED absorbs a part of the photons emitted by the light source and emits them at a different wavelength. The non-absorbed fraction of the photons emitted by the light source and the photons emitted by the phosphor constitute the output spectrum of the coated device. This approach can be implemented by easy fabrication techniques and can provide better color stability as the aging rate is determined by only one emitter. The efficiency of such a device is limited by the efficiency of the blue OLED. White light-emitting devices based on an inorganic blue LED and on down-conversion by phosphor were first published by Schlotter *et al.* [Schl97] and are widely used in existing products. Duggal *et al.* were the first to implement the idea to the field of OLEDs generating white light by combining a blue OLED with a down-conversion phosphor system [Dugg02]. Based on this approach, an illumination quality lighting panel with a power efficiency of 15 lm/W at a luminance of 1000 cd/m² was demonstrated in 2005 [Dugg05].

1.2. Content of this Work

Organic white light-emitting devices based on phosphor down-conversion are focus of the present work. Thereby two important aspects of this approach to generate white light are considered in detail: The improvement of the underlying blue OLED and the optical interaction between the OLED and the down-conversion layer.

Contemplating down-conversion devices, the underlying blue OLED does not only determine the efficiency of the light source but also its price. Hence, to utilize down-conversion OLEDs for low cost general lighting applications, a simple and cheap solution based processing approach is desirable, provided the efficiency of devices is not compromised. Highly efficient solution processed blue electrophosphorescent organic light-emitting diodes based on a simple bi-layer structure are reported in chapter 3. Therefore a phosphorescent dye

and a non-conjugated polymer host, molecularly doped with electron transporting molecules, are utilized. Furthermore, the evolution of device efficiency for this class of OLEDs is studied. Thereby the contribution of charge balance within the emissive layer and optical effects are analysed and determined quantitatively.

An advantageous side effect of a down-conversion layer applied on the substrate surface of a blue OLED can be light extraction enhancement due to light scattering by phosphor particles. In general, the modification of the light emitting surface is a well known approach to increase the external efficiency of OLEDs [NakaT04], [Shia04a], [Shia04b]. A general method to evaluate substrate surface modifications for light extraction enhancement of OLEDs is proposed in chapter 4. This method is experimentally demonstrated using green electrophosphorescent OLEDs whose substrate surface was modified by applying a prismatic film to increase light outcoupling from the device stack.

Using the evaluation method proposed in chapter 4, down-conversion OLEDs are studied from an optical point of view in chapter 5. Therefore the physical processes occurring in the down-conversion layer are translated into a ray-tracing simulation. The simulation model is confirmed by comparing its predictions to experimental results. Based on results obtained from ray-tracing simulation, some of the implications of the model for the performance of down-conversion OLEDs are discussed. In particular it is analysed how the resultant reflectance of the underlying blue OLED and the particle size distribution of the phosphor powder embedded in the matrix of the down-conversion layer influence extraction efficiency. Thereby room for improvement and challenges in the design of down-conversion OLEDs are identified. Finally, an approach to improve angular color homogeneity of down-conversion devices is demonstrated.

2. Theory and Fundamentals

In this chapter the theory and fundamentals of this work are outlined. As to the devices used for the investigations of the following chapters, the functionality and structure of OLEDs are reviewed. Next, light out-coupling from OLED devices is described. Thereby the role of optical half cavities formed by OLEDs is depicted. One further aspect described is the physiological sensation of light in terms of the measurements required in lighting technology. Furthermore, the principle of the generation of white light by means of luminescence conversion is explained, whereby a survey of previous work on down-conversion OLEDs is given. With regard to the physical processes in a down-conversion layer containing phosphor particles, the theoretical basics of absorption and scattering by small particles are outlined.

2.1. Structure and Functionality of OLED Devices

2.1.A Organic Materials for Light Emitting Devices

Low molecular weight materials (so-called *small molecules*) and conjugated polymers are the two major classes of organic materials in OLED-technology. Both classes have in common a conjugated π -electron system formed by the p_z -orbitals of sp^2 -hybridized C-atoms in the molecules. The delocalized π -bonds are significantly weaker than the σ -bonds which form the backbone of the molecules. Hence, the lowest electronic excitations of conjugated molecules are the transitions between the bonding π and anti-bonding π^* orbitals. Typically, the energy gap of the π - π^* transition is in the range of 1.5 and 3 eV, which leads to light absorption or emission in the range of the visible spectrum. The terms HOMO and LUMO are usually used for the *highest occupied molecular orbital* and the *lowest unoccupied molecular orbital*.

From the processing point of view, one important difference between the two classes of materials is given by the way how they are processed to form thin films. Whereas small molecules are usually deposited from the gas phase by evaporation, conjugated polymers can

only be processed from solution e.g. by spin-coating or printing techniques. In contrast to small molecule OLEDs (sm-LEDs), polymer OLEDs (PLEDs) are usually restricted to a bi-layer structure. Here the application of further polymer layers would lead to dissolution of the underlying organic layers, due to the existence of only two kinds of solvents (polar and non-polar).

2.1.B Physical Processes in an OLED

In the simplest case an OLED comprises an organic *emission layer* (EML) embedded in between two electrodes. At least one of the electrodes is transparent to enable light outcoupling from the device. Fig. 2-1 shows the typical stack structure of such a device, where indium tin oxide (ITO) is used as a transparent anode applied on a transparent substrate. Under an applied electric field electrons and holes are injected from the cathode and the anode respectively, into the organic layer(s), where the charge carriers move towards each other. If the Coulomb interaction energy between an electron and a hole is higher than the average thermal energy, the electron-hole capture takes place and they can form an excited state, the *exciton*. The decay of an exciton can lead to the emission of a photon.

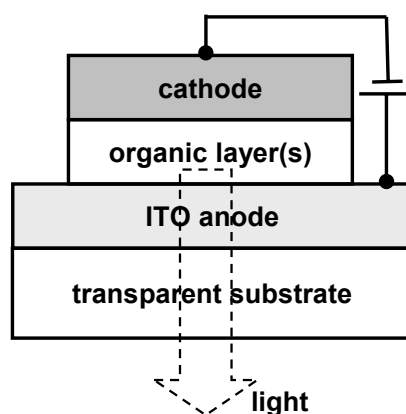


Fig. 2-1. Scheme of OLED structure.

In the simple OLED described above the work functions of both electrode materials and the HOMO and LUMO of the organic material used for the emission layer have to be adapted to each other in order to maximize the number of injected electrons and holes (see Fig. 2-2). Furthermore, the organic materials should have a sufficient high conductivity for

both types of charge carriers to enable the recombination of as many as possible holes and electrons. This is why OLED devices usually comprise two or more organic layers having different charge transport properties and different energy levels. Hence, electronic and optical properties can be optimized separately for each layer.

Fig. 2-2 illustrates the functionality of an OLED in the case of a bi-layer device. Here atop of the anode an organic *hole transport layer* (HTL) is applied, followed by an organic *electron transport layer* (ETL), which is also the emission layer (EML) at the same time. The functionality can be divided into various physical processes which are in particular:

- charge injection (I)
- charge transport (T)
- electron-hole capture and exciton formation (E)
- diffusion of excitons (D)
- decay of excitons (Ph)

These physical processes will be explained more in detail in the following.

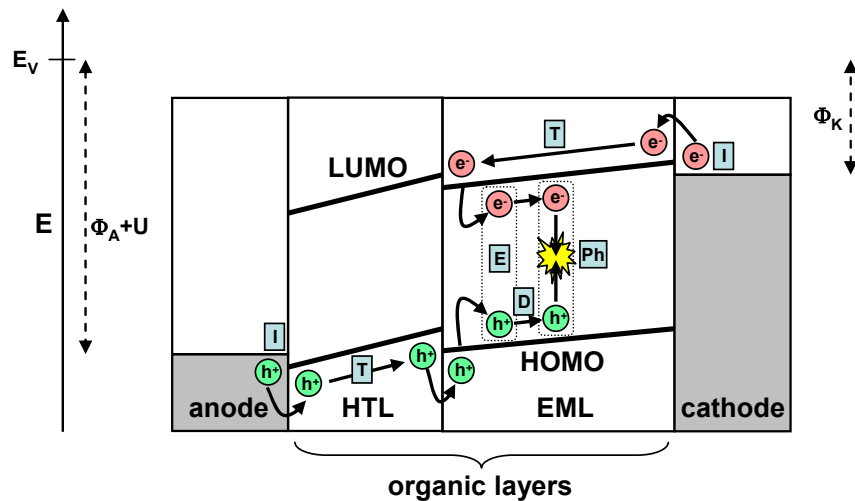


Fig 2-2. Physical Processes in a bi-layer OLED: Injection (I) of charge carriers (h^+ and e^-) at the electrode-organic interfaces; charge transport (T) driven by the applied field; recombination and exciton formation (E); exciton diffusion (D); radiativ decay of excitons (Ph). The work functions of both electrode materials (Φ_A and Φ_K) and the HOMO and LUMO of the organic materials used for the HTL and the EML, respectively, are adapted to each other. E_V stands for the vacuum energy level.

Charge Injection (I)

Injection of charge carriers from the electrodes is, essentially, one of the processes governing device operation. This requires low energetic barriers at the electrode-organic interfaces for both contacts to inject equally high amounts of electrons and holes, which is required for a balanced charge flow. Thus the difference between the work function of the cathode material and the energy level of the corresponding LUMO on the one side and the difference between the work function of the anode material and the corresponding HOMO on the other side should be minimal in order to avoid limitation of charge injection by energetic barriers. Considering state of the art OLED devices, these differences are usually very small due to the development of appropriate organic materials. Ideally, the contacts at the interfaces are *ohmic*, where the energetic differences are smaller than 0.3 eV [Stau99], [Stös99]. In this case space-charge limitation¹ of the current comes into play.

In literature there are various models describing injection theoretically. Thermoionic injection, tunnelling injection and - as a combination of both theories - thermoionic field injection are models derived from physics of inorganic semiconductors. Arkhipov *et al.* developed a model of charge injection considering the charge transport in organic materials [Ark98]. This model is based on a spatial and energetic distribution of allowed states within the organic bulk, which can be reached from the Fermi-level of the electrode by a hopping-mechanism.

Materials having a low work function such as calcium ($\Phi_{\text{Ca}} = 2.9$ eV) or barium ($\Phi_{\text{Ba}} = 2.7$ eV) are suitable for the injection of electrons. Thin layers (≈ 1 nm) of halogen salts of alkali metals such as lithium fluoride or caesium fluoride can be used [Brow00] alternatively. In both cases the cathode has to be protected by a more stable metal layer (aluminum or silver for example) in order to prevent degradation of the cathode and to ensure a sufficient electric contact.

Materials having a high work function are required for the anode. In OLED technology the most common anode material is ITO ($\Phi_{\text{ITO}} = 4.5\text{-}5.0$ eV, sheet resistance $\leq 20 \Omega/\square$ for a 100 nm ITO layer on a glass substrate [Kim98]). The use of ITO enables light outcoupling through the anode, due to the high transparency of ITO ($\approx 90\%$) within the full range of the visible spectrum. ITO is a non-stoichiometric composition of indium and tin (90:10). Its transparency, conductivity and work function depend on process

¹ In the case of ohmic contacts charge injection is not limited by the energetic barrier between the organic material and electrode material. Here injection is limited by the charge carriers within the device, which shield the applied electric field partly.

conditions. For example, the work function can be increased by 0.5 eV using a UV-ozone treatment or an oxygen plasma [Mill00].

Charge Transport (T)

When transport of electrons or holes in an organic molecular solid is considered, one has to bear in mind that this involves ionic molecular states. E.g., in order to create a hole, an electron has to be removed to form a cation M^+ out of a neutral molecule M . This so called defect electron can then move from one molecule to the next. In the same way electron transport involves negatively charged ions M^- . When considering polymers, the charged states are usually termed positive or negative *polarons*. The transfer of one polaron from one polymer chain to the next or from one small molecule to the next can be interpreted as a *hopping* mechanism [Scot00]. For both classes of materials the mobility of charge carriers is determined by the hopping mechanism from donor-sites to acceptor-sites [Kins00], [Baes93]. This transfer can be seen as a redox-reaction. The corresponding activation energy is dependent on temperature and the electric field. Baessler *et al.* developed a theoretical description of the charge carrier mobility in an amorphous organic solid, which can be applied on small molecules and conjugated polymers [Baes93]:

$$(Eq. 2-1) \quad \mu(E, T) = \mu_0 \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\right] \exp\left[C\left(\left(\frac{\sigma}{k_B T}\right)^2 - \Sigma^2\right)\sqrt{E}\right],$$

where μ_0 is the zero-field mobility in the limit $T \rightarrow \infty$, Σ gives the geometrical disorder and σ the Gaussian density of states. The constant C describes the average intersite spacing. E is the electric field, T is the temperature and k_B is the Boltzmann-constant. Here each site which can be represented by a molecule has an individual energetic band position.

Traps, which are favoured sites due to a lower energetic level, strongly affect the charge transport properties of an organic solid, since trapped charge carriers do no longer take part in the charge transport. However, their columbic charge will influence the electric field distribution in a device and therewith the transport of other charge carriers. Especially in doped systems, where a second material is added into an organic material, a lower HOMO or LUMO-level can lead to the formation of traps. By the right choice, traps can improve the charge transport.

In the solution processable devices presented within this work, the conjugated polymer poly(3,4)-ethylendioxythiophene (PEDOT, molecular structure see Fig. 2-3) is used

as hole transporting material. Pure PEDOT has a low conductivity in the range of 10^{-9} S/cm. By doping with poly(styrene sulfonate) (PSS), the conductivity can be increased up to 10^2 S/cm [Reha03]. Typical polymeric emitter materials, which act as electron transporting material at the same time, are poly(p-phenylenvinylene) [Burr90], polyfluorene [Bern00] and polyspiros [Beck01].

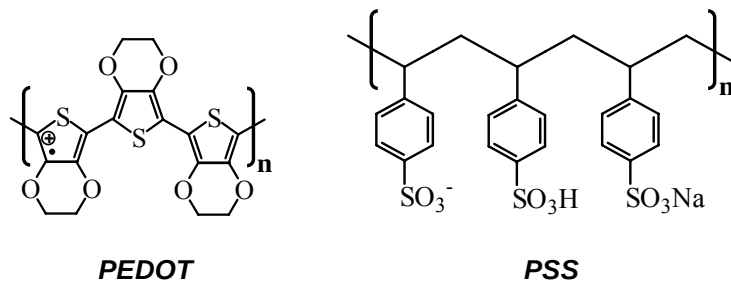


Fig. 2-3. Molecular structure of PEDOT:PSS [Brüt05].

Exciton Formation and Diffusion (E&D)

Due to the electromagnetic attractive interaction electrons and holes can form excitons. Excitons may be thought of as two-electron system: one electron is excited into an unfilled orbital of a given molecule or polymer, while the second remains in a partially filled ground state. For such a system quantum mechanics gives the possible spin orientations with either $S = 0$, or $S = 1$. The $S = 0$ spin wave function is antisymmetric under particle exchange:

$$(Eq. 2-2) \quad \sigma_- = \frac{1}{\sqrt{2}} \{ \uparrow(1) \downarrow(2) - \downarrow(1) \uparrow(2) \},$$

where $\uparrow$ and $\downarrow$ represent the possible spin states of each electron. The electrons are signified by (1) and (2); “+” and “−” represent symmetric and antisymmetric spin wavefunctions. There are three possible spin wave functions with $S = 1$, all symmetric under particle exchange:

$$\begin{aligned}
 \text{(Eq. 2-3)} \quad \sigma_+ &= \frac{1}{\sqrt{2}} \{ \uparrow(1) \downarrow(2) + \downarrow(1) \uparrow(2) \} \\
 \sigma_+ &= \uparrow(1) \uparrow(2) \\
 \sigma_+ &= \downarrow(1) \downarrow(2)
 \end{aligned}$$

The degeneracy of the states is given by their titles: the $S = 0$ state is denominated as a *singlet*, and the $S = 1$ as a *triplet*. In an electroluminescent device, charge carriers are injected from the electrodes with random spin orientation. These random spin orientated carriers lead to a 1:3 singlet:triplet ratio, i.e. the fraction of singlet excitons is $\chi_s = 0.25$.

The lifetime of an exciton is in the range of a few ns for a singlet and a few ms for a triplet [Pope92]. During their lifetime excitons can diffuse within the organic bulk. Here two transport mechanisms are known: Radiative and non-radiative transfer: The range of the radiative transfer (i.e. sequences of emission and absorption) is a few 10 nm. However, the radiative transfer plays a minor role. The non-radiative transfer can be divided into Förster- and Dexter-transfer. Förster transfer is based on dipole-dipole interaction and its range is a few nm [Förs48]. In the case of the Dexter transfer an intermolecular electron exchange takes place (range: ≈ 1 nm) [Dext53]. A detailed description of energy transfer mechanisms is given in reference [Hunz03].

Exciton Decay (Ph)

The exciton spin plays an important role because it defines if the decay of an exciton can be radiative in a fluorescent material. The ground state of most molecules is a singlet state. And as the emission of a photon conserves the symmetry of the spin wave function, typically only singlet excited states can decay to the ground state and emit light. Radiative singlet decay is denominated *fluorescence*. Radiative triplet decay is denominated *phosphorescence*. However, in general the probability of luminescence from triplet states is so low, leading to almost all their energy being lost to non-radiative processes, for example to triplet-triplet annihilation by generation of thermal energy. Thus a fundamental limit on the efficiency of fluorescent organic materials is given by the excitonic singlet-triplet ratio. Consequently, $1/\chi_s$ expresses the gain in efficiency if luminescence can be generated by the radiative decay of triplets as well.

Though radiative triplet decay is rare, the process can be very efficient in certain materials. For instance, the decay of the triplet state is partly allowed if the excited states are

mixed in such a way that the triplet attains some singlet character. Singlet-triplet mixing and efficient phosphorescence is achieved in molecules with large spin-orbit coupling due to the presence of heavy metal atoms such as platinum or iridium (*ISC- inter system crossing*). In order to make use of an efficiently phosphorescent material in an OLED device, the transfer of both singlet and triplet excitons from the charge transport layer (henceforth termed as *host*) to the phosphorescent emitter (*guest*) has to be ensured [Bald04].

Since the beginning of OLED technology scientists have preferred to separate the functions of charge transport and luminescence within the emission layer of the device. This can be achieved by mixing a small amount of a highly luminescent phosphorescent guest into a host material with appropriate charge transport abilities. This technique confines excitons on phosphorescent guest molecules, which leads to the advantageous effect of the minimization of competing non-radiative processes, such as exciton-quenching [Bald00a] by other excitons in the emissive material, by charges in the emissive materials and by metallic contacts. The overall efficiency of energy transfer between host and guest is determined by four processes, as shown in Fig. 2-4 [Bald00b]: the rates of exciton relaxation on the guest and host, k_G and k_H respectively; and the forward and reverse triplet transfer rates between guest and host, k_F and k_R respectively.

Host-to-guest triplet energy transfer is endothermic when the free energy change $\Delta G > 0$, and exothermic when $\Delta G < 0$. In the case of fluorescent materials, endothermic energy transfer is very inefficient and leads to a large population of excitons remaining confined on the host, where they rapidly decay in fluorescent or non-radiative. But endothermic energy transfer may be successfully applied in phosphorescent devices, since the decay of excitons in the host is retarded by spin conservation, i.e. $k_G \gg k_F \gg k_H$.

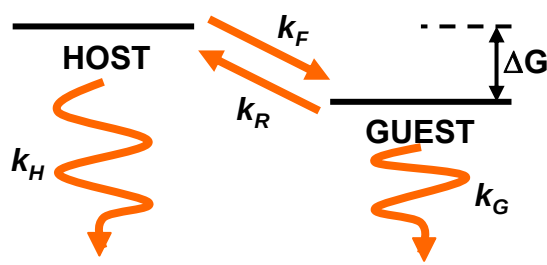


Fig. 2-4. Triplet dynamics in a guest-host system: the rates of forward and back transfer, k_F and k_B respectively, are determined by the free energy change (ΔG) and the molecular overlap; also significant are the rates of decay from the guest and host triplet states, labelled k_G and k_H respectively. Adapted from [Bald00b],[Brüt05].

Resulting Efficiency

In general, the resulting external quantum efficiency of an OLED device, η_{ext} , is given by [Adac01b]:

$$(Eq. 2-4) \quad \eta_{ext} = \gamma \eta_{ex} \phi_p \eta_{ph}$$

Here η_{ex} is the fraction of total formed excitons which result in radiative transitions ($\eta_{ex} = 1/4$ for fluorescent materials, and 1 for purely phosphorescent materials). γ is the ratio of electrons to holes injected from opposite contacts (the electron-hole charge-balance factor), which is ideally equal to 1. ϕ_p is the intrinsic quantum efficiency for radiative decay (including both fluorescence and phosphorescence) and η_{ph} is the total photon extraction efficiency out of the device into the ambient. Light extraction from OLED devices will be explained more in detail in chapter 2.2 and is one major topic of this work.

In the field, the power efficiency [lm/W] and current efficiency [cd/A] are further magnitudes describing device efficiency. These photometric efficiencies considering the spectral sensitivity of the human eye will be defined in chapter 2.3.

In both technologies, polymeric OLEDs and small molecule OLEDs, the typical quantum efficiency of state-of-the-art devices based on fluorescent materials is in the range of 5%. In literature green emitting phosphorescent OLEDs (PHOLEDs) with external quantum efficiencies approaching 20% and power efficiency on the order of 70-80 lm/W have already been reported [Adac01b], [Ikai01].

2.1.C Device Structure and Fabrication

In the devices reported in this work, the OLED concept was realized by means of a standard bottom-emitter structure². Fig. 2-5 shows the general structure of such devices. Here the transparent ITO-anode enables outcoupling of the light generated in the light emitting polymer layer (LEP) through the glass-substrate.

The PLEDs used for the experiments presented in this work were fabricated as follows. The deposition of the OLED-layers was performed on ITO-coated float-glass

² In general there are three types of OLED structures distinguished by the side of light emission. In the case of a bottom emitting OLED (*bottom emitter*) light is emitted through a transparent substrate. Light generated in a top-emitting OLED (*top emitter*) is outcoupled through a transparent encapsulation or passivation layer. *Transparent OLEDs* having two transparent electrodes emit light from both sides.

substrates. The glass substrate had a thickness of 0.7 mm and a refractive index of $n = 1.52$. The thickness of the ITO layer was in the range between 120 nm and 130 nm. The ITO layer was patterned using standard photolithographic techniques. This was followed by cleaning of the ITO surface including wash steps with deionized water. In addition, the ITO substrates were subjected to oxygen plasma treatment for 10 minutes, which leads to additional cleaning and an increase of the ITO work function. Furthermore, due to the plasma treatment the surface energy of the ITO layer is increased, which improves its wettability. As hole transport layer a thin film of PEDOT:PSS was spin coated atop the ITO. The LEP was then spin coated on the top of the PEDOT:PSS, followed by thermal evaporation of the cathode layers comprising caesium fluoride (CsF) or barium (Ba) and aluminum (Al). Following evaporation of the cathode, the devices were encapsulated with a glass lid and getter³, in order to prevent the organic layers and the reactive cathode layer from being degraded by moisture and oxygen. All device fabrication steps from the LEP spin coating to device encapsulation were carried out in an inert nitrogen atmosphere. In the devices presented in chapter 4 additional organic layers are deposited between the LEP and the cathode by using evaporation. Detailed description of device materials and layer thicknesses of the different devices used within this work are given in the corresponding chapters. In the study of chapter 5.2.C a series of sm-LEDs were used as underlying blue light sources in down-conversion devices. A brief description of device fabrication is given there.

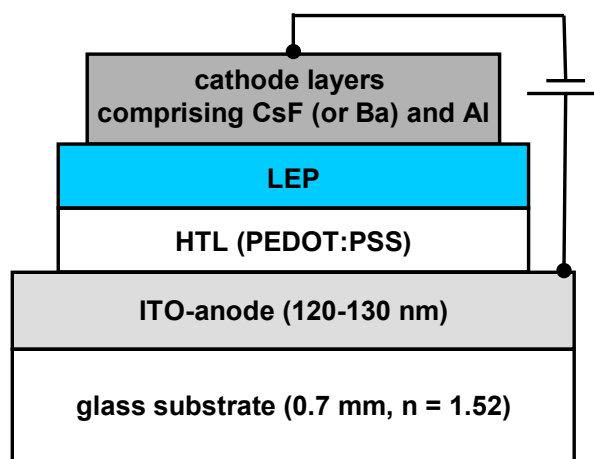


Fig. 2-5. Schematic structure of the devices used within this work.

³ The getter comprises a certain type zeolite which functions as a drying agent. This zeolite effectively absorbs and accumulates moisture.

2.2. Theoretical Description of OLED Half Cavities

2.2.A Light Outcoupling from an OLED Device

Due to the mismatch of the refractive index between air and the organic stack of an OLED, only a fraction of the photons generated within the device is extracted to air. Total internal reflections into wave guiding modes and self absorption are two mechanisms reducing external device efficiency. In the following paragraph the outcome of photons emitted at various internal angles θ_{em} within the organic layer is reviewed with regard to a standard bottom emitter structure (Fig. 2-6). This organic layer is bounded on one side by the metal and the other by the ITO-glass substrate having an interface with air. The emission can be divided into various angular zones:

- *Surface emission zone:* $0 \leq \theta_{em} < \theta_{c1}$. $\theta_{c1} = \sin^{-1}(n_a/n_e)$ is given by Snell's law, where n_a and n_e are the refractive indices of air ($n_a = 1.00$) and the emitter layer. These photons are emitted within the surface-escape cone and will emerge through the surface (*external mode*).
- *Substrate wave-guided zone:* $\theta_{c1} \leq \theta_{em} < \theta_{c2} = \sin^{-1}(n_g/n_{ITO})$, where n_g is the refractive index of the glass substrate and n_{ITO} is the refractive index of the ITO. These substrate-mode photons are confined by metal reflection and total internal reflections at the surface of the substrate (*substrate wave-guided mode*). A fraction of these substrate mode photons can emerge through the edge after a number of reflections.
- *Anode/organic wave-guided zone:* $\theta_{c2} \leq \theta_{em} < 90^\circ$. These photons are wave-guided along the emitter-ITO layer (*anode/organic wave-guided mode*). This occurs because $n_{ITO} \approx 1.85$ (at 550 nm wavelength) is higher than n_g and usually higher than n_e . At least one TE and TM mode are supported by a 100-200 nm thick ITO and 80-120 nm organic layer. The wave-guiding is, however, very lossy with an absorption coefficient of the order of 5000 cm^{-1} due to the ITO, the metal and the organic layers [Kim99].

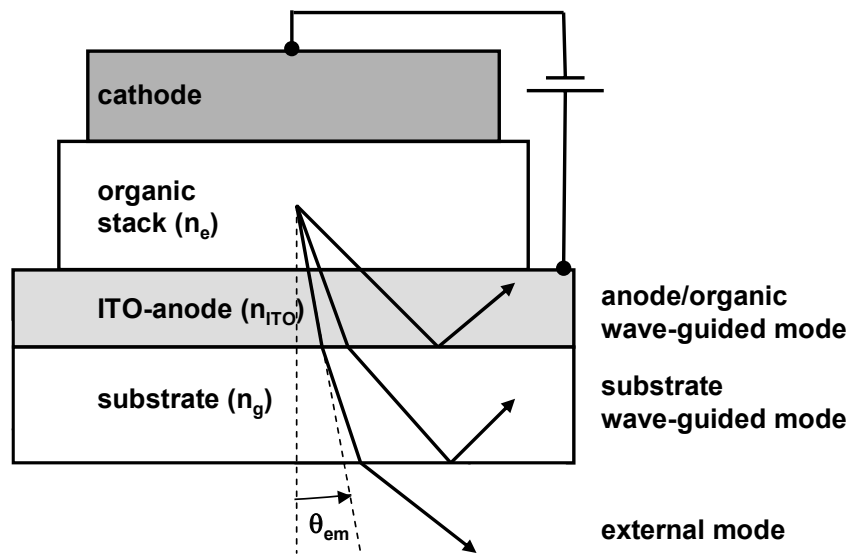


Fig. 2-6. The external mode, the substrate wave-guided mode and the anode/organic wave-guided mode in an OLED device. Dependent on the emission angle θ_{em} the photons generated in the organic stack are outcoupled or wave-guided.

In the thin-film structure of an OLED the radiative decay of excitons within the light emitting layer takes place physically close to the metallic cathode. As a consequence of reflection at the cathode, the rate and direction of emission are strongly affected by optical interference effects. To illustrate this, a perfect mirror is considered, which is placed close to a punctual emitter. This emitter is embedded in the planar layer of a medium having the refractive index n_e . Here photons generated by the emitter escape only into air for directions contained in a cone with an apex of $2\theta = \sin^{-1}(1/n_e)$. If the wave emitted towards the anode and the reflected wave interfere constructively within the entire escape cone, an increase in light extraction might be achieved. By contrast, destructive interference results in inhibition of emission perpendicular to the mirror plane. These interference effects strongly depend on the distance between the punctual emitter and the mirror. Consequently, in an OLED-device the distribution of the light into the external mode, the substrate wave-guided mode and the anode/organic wave-guided mode is determined by the location of the emission zone and the device architecture, respectively. In contrast to an inorganic resonant full cavity LED [Schu94], the architecture of a standard OLED (bottom emitter with reflecting cathode and ITO anode) results in the formation of a so-called half-cavity because only the metal electrode acts as a real mirror.

2.2.B The Half-Space Model

In this section the half-space model [Kim00] is outlined, which is used for the optical simulations presented within this work. The radiative emission from the recombining excitons is modelled by oscillating dipoles in front of a mirror, as shown in Fig. 2-7 [Björ94], [Craw88]. These dipoles are embedded inside the organic half-space at a distance z from the cathode reflector. The other half-space is occupied by the metal. For a sheet of dipoles at distance z (corresponding to a phase distance $\delta = 2 \pi n_e z / \lambda$) from the cathode-reflector, the internal emission intensity I_{em} varies with the internal emission angle θ_{em} as:

$$(Eq. 2-5) \quad I_{em}(\theta_{em}, \lambda, z) \propto |1 + r_s \exp(i 2 \delta \cos \theta_{em})|^2 + \cos^2 \theta_{em} |1 - r_p \exp(i 2 \delta \cos \theta_{em})|^2$$

for an ensemble of in-plane dipoles, and as

$$(Eq. 2-6) \quad I_{em}(\theta_{em}, \lambda, z) \propto |1 + r_s \exp(i 2 \delta \cos \theta_{em})|^2 + |1 - r_p \exp(i 2 \delta \cos \theta_{em})|^2$$

for an ensemble of isotropic dipoles. Here r_s (and r_p) is the Fresnel reflection coefficient for the s-(p-) polarization, n_e is the effective refractive index of the organic materials between the sheet of dipoles and the cathode-reflector and λ is the emission wavelength in vacuum. The first and the second term on the right-hand side separately describe the modified s- and p-wave vacuum fields at the dipole location. In the model the exciton profile $E(z)$, which is the local distribution of excitations within the emissive layer, is interpreted as a distribution of dipole sheets (Fig. 2-7).

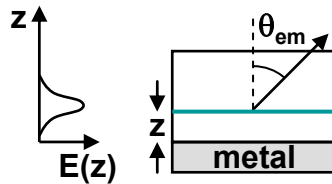


Fig. 2-7. Schematic diagram of the half-space optical model. The dipoles are embedded inside the organic half space. $E(z)$ is the distribution of dipole sheets, which is the representation of the exciton profile within the emissive layer.

To obtain the external emission intensity and the intensity in the substrate respectively, Fresnel transmittance and optical refraction are considered. When light is transmitted from one medium to another, the transmitted intensity $I_2(\theta_2)$ is in general related to the incident intensity $I_1(\theta_1)$ by

$$(Eq. 2-7) \quad I_2(\theta_2) = I_1(\theta_1) T(\theta_1) \frac{n_2^2 \cos \theta_2}{n_1^2 \cos \theta_1}$$

where θ_1 and θ_2 are related by Snell's law

$$(Eq. 2-8) \quad n_1 \sin \theta_1 = n_2 \sin \theta_2$$

and $T(\theta_1)$ is related by the respective Fresnell transmission coefficients (t_s and t_p)

$$(Eq. 2-9) \quad T(\theta_1) = \frac{n_2 \cos \theta_2}{n_1 \cos \theta_1} t_{s(p)}^2$$

The internal photon flux emitted by a distribution of dipole sheets into the external mode F_{ext} and the flux emitted into the substrate wave-guided mode F_{subs} are calculated according to Eqs. 2-10 and 2-11 respectively.

$$(Eq. 2-10) \quad F_{ext} = \int_{z=0}^{z=d} \int_{\theta_{em}=0}^{\theta_{em}=\theta_{c1}} \int_{\lambda=0}^{\lambda=\infty} E(z) I_{em}(\theta_{em}, \lambda, z) 2\pi \sin \theta_{em} d\lambda d\theta_{em} dz$$

$$(Eq. 2-11) \quad F_{subs} = \int_{z=0}^{z=d} \int_{\theta_{em}=\theta_{c1}}^{\theta_{em}=\theta_{c2}} \int_{\lambda=0}^{\lambda=\infty} E(z) I_{em}(\theta_{em}, \lambda, z) 2\pi \sin \theta_{em} d\lambda d\theta_{em} dz$$

Here I_{em} is weighted by the emission spectrum of the emitter in a space filled with the emitting medium without any interfaces, $EL_0(\lambda)$. $EL_0(\lambda)$ corresponds to the photoluminescence (PL) spectrum of the emission layer.

The micro cavity simulation tool *UniMCO 4.0* by UniCAD [Unic], which was used for the optical simulations of PHOLEDs presented in the chapters 3 and 4 of this work, is based on the model described above. Using the transfer matrix formalism [Arwi00], further

refinements are implemented, which are based on the optical constants as a function of wavelength of all layers.

In the presented PHOLEDs light-emitting molecular dyes are diluted into a polymer matrix. Here no orientation of the dyes is expected. Thus, in the corresponding calculations the oscillating dipoles are set to be isotropic.

Considering Eq. 2-5, it is obvious that the variation in the location and shape of the exciton profile $E(z)$ formed within the LEP can result in significant differences in the extent to which light can be outcoupled from the device due to the presence of a half-cavity in the OLED stack. It is also evident that such half micro cavity effects can lead to changes in the observed electroluminescence (EL) spectrum, as light corresponding to different wavelengths is extracted to the ambient to a different extent for a given location of the emission zone.

Furthermore the simulation tool allows the determination of the emission spectrum of the emitter in an unbounded medium, $EL_0(\lambda)$. $EL_0(\lambda)$ can be extracted from experimental data, using the EL-spectrum of the device measured in the direction normal to the device substrate, and performing numerical back calculation based on the model described above.

2.3. Physiological Sensation of Light

In this section a survey of vision, photometry, and colorimetry is given in terms of the basic topics that are most relevant for the understanding of the present work. More details can be found in specialized books ([Rich76], [Coat97], [Wysz00], [Rea00]) or in the International Commission on Illumination (Comission Internationale de l'Éclairage, CIE) Technical Report Colorimetry [CIE04].

2.3.A Human Vision

Lighting technology is strongly related to the properties of human vision. These properties determine the quantity and the quality requirements for lighting. The primary processes of vision take place in the eye, where the image is projected on the *retina*. The retina consists of detector cells (receptors), where the energy of light is converted into nerve impulses. There are two types of receptors, *rods* and *cones*. Rods have higher sensitivity and are important in night vision, when the eye has to adapt to darkness (*scotopic vision*). But rods are not able to distinguish between colors because they contain only one type of photopigment.

Under high luminance, the response of rods is saturated. In this case vision is mediated entirely by cone receptors (*photopic vision*). There are three types of pigments, which may be contained in the cones: erythrolabe (L-type or long-wavelength cones), chlorolabe (M-type, middle-wavelength cones), and cyanolabe (S-type, short-wavelength cones). These photopigments allow the distinction of colors since they have different spectral sensitivity. As different photoreceptors take part in the process of vision, the spectral sensitivities of scotopic vision and overall photopic vision differ. The maximum of scotopic sensitivity, which is given by the photoresponse of rods and the transmittance of pre-retinal media, is in the blue-green region at a wavelength of 507 nm in air. The photopic sensitivity peaks in the yellow-green region at a wavelength of 555 nm in air.

From the point of view of lighting technology, photopic vision is the most important as most human activities take place under high luminance. This is why much effort has been dedicated to the calibration and digitalization of the spectral response and *color* resolution of photopic vision. In 1924, the CIE introduced the relative *luminous efficiency function*, $V(\lambda)$, for photopic vision. The function $V(\lambda)$ is defined in the range between 380 and 780 nm. This wavelength interval is defined as the *visible spectrum* [Rea00].

2.3.B Photometry

Light is electromagnetic radiation. *Radiometry* measures the quantities related to radiant energy. These quantities are denominated as radiant and their units refer to energy (joules). For instance, the radiant flux Φ_e is the time rate of flow of radiant energy measured in watts; the radiant intensity $I_e = d\Phi_e/d\omega$ (W/sr) is the radiant flux per unit solid angle in a given direction. *Photometry* deals with the visual sense of brightness. Consequently, photometry differs from radiometry in its consideration of visual response. The relevant quantities in photometry are denominated as luminous. The luminous flux, Φ_v , is linked to the spectral density of the radiant flux, $\Phi_{e\lambda}$, $d\Phi_e/d\lambda$ (also termed as spectral power distribution, $S(\lambda)$) by the 1924 CIE luminous efficiency function $V(\lambda)$. The luminous flux is measured in lumens (lm):

$$(Eq. 2-12) \quad \Phi_v = 683 \text{ lm/W} \cdot \int \Phi_{e\lambda} V(\lambda) d\lambda$$

Here the integral is extended over the entire visible spectrum. Hence, the luminous intensity I_v is the luminous flux from a point source per unit solid angle:

$$(Eq. 2-13) \quad I_v = d\Phi_v / d\varpi = 683 \text{ lm/W} \cdot \int I_{e\lambda} V(\lambda) d\lambda,$$

where $I_{e\lambda} = dI_e/d\lambda$ is the spectral density of the radiant intensity. The unit of luminous intensity is candela (cd) or lm/sr.

The concept of luminous intensity cannot be applied to an extended light source which cannot be regarded as a point source. Such sources are characterized by *luminance*, which is the quotient of the luminous flux propagating from an element of the surface dA and observed at an angle φ per unit solid angle:

$$(Eq. 2-14) \quad L = d^2\Phi_v / (d\varpi dA \cos \vartheta) \equiv dI_v / dA',$$

where dA' is the area projected in the direction of the observation. The unit of luminance is candela per square meter (cd/m²). Sources of a higher luminance appear brighter than those of lower luminance.

Luminous efficiency and current efficiency are introduced in order to describe how efficient the source is in converting the energy and, accordingly, the applied current to light. The *luminous efficiency* (also termed as *power efficiency*) is the ability of the source to convert the consumed power P into actuation of the vision:

$$(Eq. 2-15) \quad \eta_v = \Phi_v / P$$

Luminous efficiency is measured in lm/W and is not to be confused with *luminous efficacy*, which is the measure of the ability of the radiation to produce a visual sensation and which is described by the same units. *Current efficiency* is defined for extended light sources and describes the efficiency in the conversion of applied current into actuation of the vision. Current efficiency is given by the ratio between luminance and current density and is measured in cd/A:

$$(Eq. 2-16) \quad \eta_j = L / j,$$

where j is the current density within the active area of the device.

2.3.C Colorimetry

Measurements of color are the focus of *colorimetry*. A numerical description of colors is based on a very simplified model of human vision. Therefore this description might disagree with certain subjective observations. However, the basic concepts of colorimetry are well formulated at present and are of crucial importance in describing light sources for lighting applications.

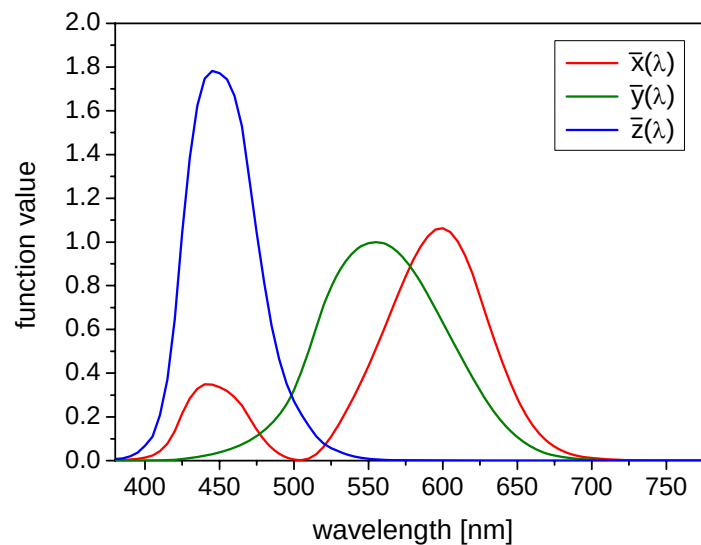


Fig. 2-8. The CIE-color-matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ of the ideal observer.

Tristimulus values were introduced in order to describe colors by certain numbers. These tristimulus values were derived from the experimental fact that most colors can be accurately imitated by a combination of not more than three appropriate primary colors (stimuli), such as red [R], green [G], and blue [B]. This allows specifying colors in amounts of the three stimuli. However, some colors, which are close to *monochromatic*, cannot be described by using only positive amounts of the three stimuli (i.e. by [R], [G] and [B]). Here negative amounts are required (color subtraction). This inconvenience was eliminated by the introduction of the imaginary stimuli [X], [Y], and [Z]. The tristimulus values X , Y , and Z (i.e., the amounts of each stimuli in a color represented by a certain spectral distribution $S(\lambda)$) are obtained by integrating the spectrum with the standard *color-matching functions* $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ representing the characteristic of an ideal observer (introduced by CIE in 1931 and shown in Fig. 2-8):

$$\begin{aligned}
 \text{(Eq. 2-17)} \quad X &= \int \bar{x}(\lambda) S(\lambda) d\lambda, \\
 Y &= \int \bar{y}(\lambda) S(\lambda) d\lambda, \\
 Z &= \int \bar{z}(\lambda) S(\lambda) d\lambda,
 \end{aligned}$$

The trichromatic system of modern colorimetry is based on the 1931 CIE Standard Observer (defined by CIE in 1931). The 1931 CIE green matching function $\bar{y}(\lambda)$ was set equal to the 1924 CIE luminous efficiency function $V(\lambda)$ for photopic vision. The chromaticity coordinates (x,y) describing the color of a light source with a spectrum $S(\lambda)$ (measured in power units) were introduced for convenience:

$$\begin{aligned}
 \text{(Eq. 2-18)} \quad x &= \frac{X}{X + Y + Z} \\
 y &= \frac{Y}{X + Y + Z} \\
 z &= \frac{Z}{X + Y + Z} \equiv 1 - x - y
 \end{aligned}$$

The third coordinate z contains no additional information. Thus the description of colors can be made by means of two chromaticity coordinates (x, y) . Fig. 2-9 depicts the 1931 CIE *chromaticity diagram* with the (x, y) coordinates of imaginary tristimulus $[X,Y,Z]$. The area embraced by the contour comprises the coordinates of all real colors. Monochromatic-color coordinates are located on a horseshoe shaped curve. A locus of points for blackbody radiators of different temperatures (Planckian locus) is shown inside the contour. The region in the vicinity of the blackbody radiator locus (starting at approximately 2500 K) defines the white color.

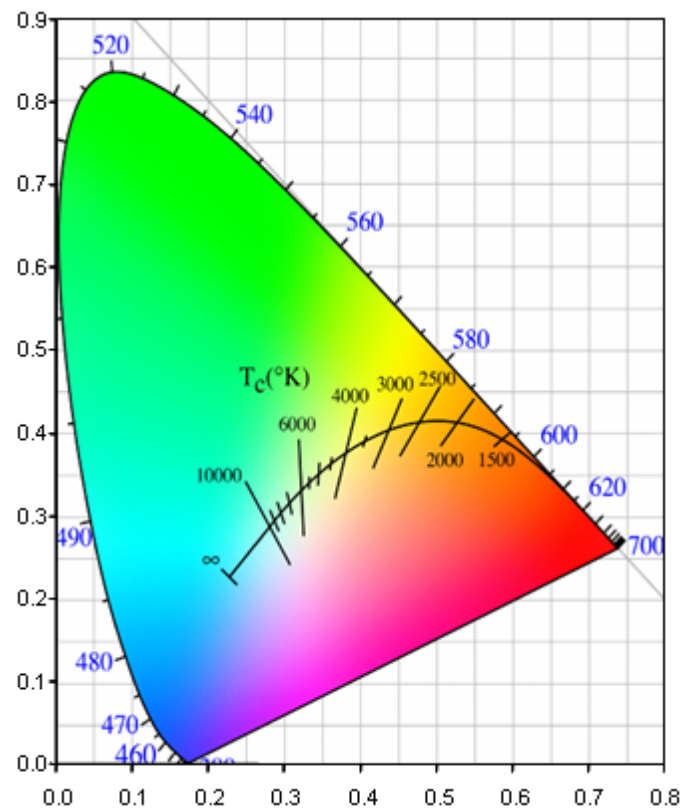


Fig. 2-9. 1931 CIE chromaticity diagram. The Planckian locus is shown by a black line, on which color coordinates related to various color temperatures are marked. Wavelengths (in nm) of monochromatic light are printed in blue.

2.4. Generation of White Light by Down-Conversion

2.4.A The Down-Conversion Concept and Luminescence Converting

Materials

The generation of white light by means of down-conversion can be achieved by combining a blue light source and one or more luminescence converting materials, also termed as *phosphors*. Phosphors absorb a fraction of the photons emitted by the light source and re-emit them at longer wavelengths. The non absorbed fraction of the photons and the photons re-emitted by the luminescence converting material(s) constitute the light emitted by the device. The appropriate amount of phosphor material has to be used to achieve the color balance for the resulting white light aimed at. Therefore the material is embedded in a transparent matrix which is applied directly on the light source or constitutes a part of the device-housing. To illustrate the down-conversion approach, Fig. 2-10 shows the EL-spectrum of a blue PLED, the absorption and re-emission spectra of a YAG:Ce³⁺ (yttrium aluminum garnet doped with cerium ions) phosphor applied on the substrate surface and the resulting spectrum of the white light emitting device (more detailed description of the device is given in chapter 5).

Generation of white light by down-conversion offers significant advantages in comparison to other approaches, where two or more emissive components provide white light (see chapter 1.1). Down-conversion devices offer better color stability as the aging rate is determined by only one emitter. The approach leads to a less complex architecture of the light source and thus can be implemented by easier fabrication techniques due to the presence of one single emitting component. Furthermore, the emission color can be controlled by adjusting the down-conversion layer without affecting the electrical properties of the underlying OLED.

Comparing the resulting efficiency of a down-conversion device to the efficiency of the underlying blue light source, the Stokes-shift due to the wavelength conversion, and the finite quantum yield of the phosphor material affect the resulting efficiency negatively. However, the photometric efficiencies (power efficiency [lm/W] and current efficiency [cd/A]) might be increased: In many cases the converted light is related to wavelengths corresponding to a higher sensitivity of the human eye (see Fig. 2-11).

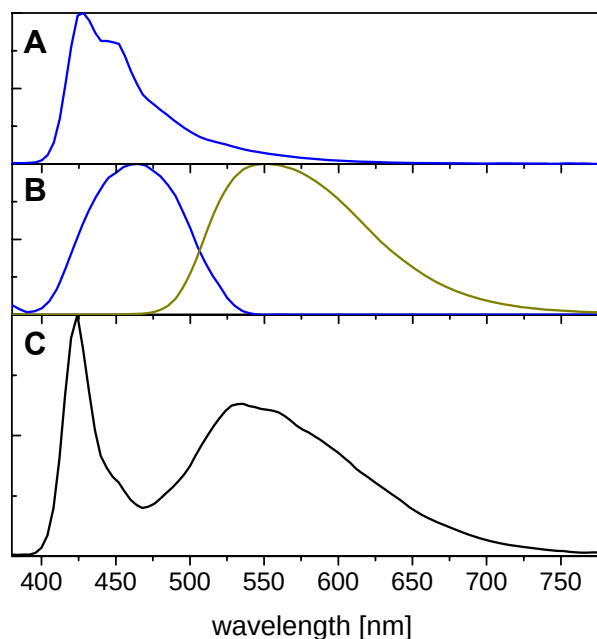


Fig. 2-10. Blue PLED emission (A) and absorption (blue line) and re-emission spectrum (yellow line) of YAG:Ce^{3+} phosphor (B). Panel C shows the resulting white spectrum obtained by down-converting the PLED emission. Absorbance and emission intensity are in arbitrary units. Phosphor data were provided by OSRAM GmbH.

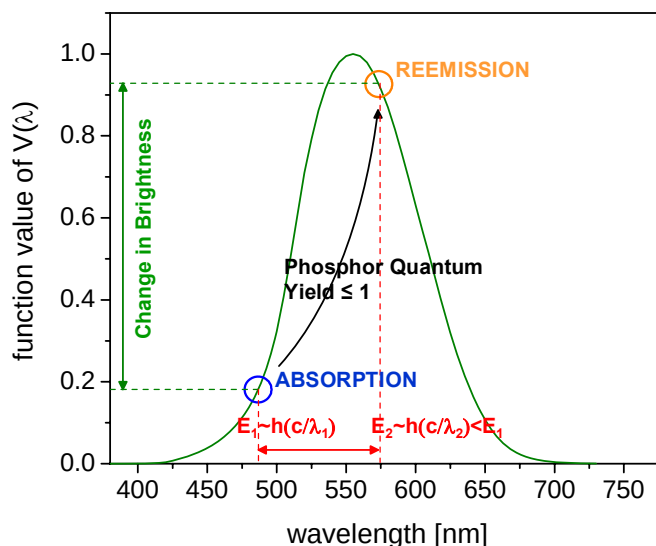


Fig. 2-11. Scheme of phosphor down-conversion. Finite phosphor quantum yield and Stokes shift affect device efficiency negatively. However, the photometric efficiencies might be increased, provided that the converted light is related to wavelengths corresponding to a higher sensitivity of the human eye (green line).

Schlottter *et al.* [Schl97] were the first who introduced the down-conversion concept into solid state lighting technology. In 1997 they demonstrated inorganic white light emitting diodes (LEDs) comprising blue emitting GaN/6H-SiC chips as primary light sources and YAG:Ce³⁺ as luminescence converting material. The YAG:Ce³⁺ particles were embedded in the epoxy resin used for the dome of the LED. The importance of YAG:Ce³⁺ is given by the fact that its spectral properties almost ideally meet the requirements for a dichromatic white LED. First, the peak of the excitation spectrum at around 460 nm coincides with the peak wavelength of the most efficient blue AlInGaN LED available (peak at 465 nm, [Muka99]). Second, the emission spectra of the phosphor fit the complementary component at 570 to 590 nm (see panel B in Fig. 2-10).

The relevant optical properties of YAG:Ce³⁺ result from allowed dipole transition between the ground-state 4f¹ and excited state 5d¹ bands. The shielded ground-state 4f¹ level is spin-orbit split. The excited state 5d¹ features strong crystal-field splitting and vibronic coupling because it is no longer shielded by the environment [Loh67]. The lowest absorption band at 460 nm is due to transitions from the lower ²F_{5/2} sublevel to the excited ²D band. The emission spectrum results from Stokes-shifted transitions from the ²D band to the ²F_{5/2} (520 nm) and ²F_{5/2} (580 nm) sublevels. At room temperature, two emission lines overlap, resulting in a structureless band [Holl69]. An important feature of the garnet is that substitution for Al³⁺ and Y³⁺ ions makes it possible to tailor the emission and excitation spectra [Holl69], [Tien73], [Naka97]. For example, the (Y_{1-a}Gd_a)₃(Al_{1-b}Ga_b)₅O₁₂:Ce³⁺ system yields the peak of the emission band in the range 510 to 580 nm and the peak of the excitation spectra in the range of 450 to 480 nm. Also, the spectral characteristics can be adjusted by the Ce³⁺ concentration [Tien73], [Bate99].

The principle of down-conversion of light sources is not restricted to inorganic garnets. Schlottter *et al.* demonstrated white light-emitting LEDs, which have been fabricated by dissolving green and red emitting perylene dyes (green dye: BASF F 083, red dye: BASF F 300) into the epoxy-dome of blue emitting GaN/6H-SiC LEDs [Schl97]. Heeger *et al.* presented a white light emitting hybrid LED with a film of the conjugated polymer poly(2,5-bis(cholestanoxyl)-1,4-phenylene vinylene) as luminescent converting material incorporated into the epoxy dome of a blue GaN LED [Hide97], [Zhan98].

The first solid-state white light-emitting device using CdS quantum dots was developed and presented at the Department of Energy's (DOE) Sandia National Laboratories in July 2003 [Sand03]. Quantum dots as a new class of luminescence converting material have been integrated with a commercial LED chip that emits in the near ultraviolet at 400 nm

by encapsulating the chip with a dot-filled epoxy creating a dome. The quantum dots in the dome absorb the invisible 400 nm light from the LED and re-emit it in the visible region.

2.4.B Previous Work on Down-Conversion OLEDs

In 1997 Leising *et al.* introduced the down-conversion concept into OLED technology [Leis97], [Niko97]. They demonstrated the realization of red, green, blue (RGB) light emission for display applications by covering a blue emitting OLED based on parahexaphenyl (PHP) (peak wavelength 425 nm) with color-converting dye/matrix layers. The blue emission was converted into green light by applying a thin film of coumarin in a poly-methyl-methacrylate (PMMA) matrix atop the OLED. The coumarin absorption spectrum efficiently overlaps with the PHP emission spectrum, so that the blue OLED emission can be efficiently absorbed and green photoluminescence re-emitted (peak 506 nm). For red light emission, a perylene dye (BASF Lumogen F300) in a PMMA matrix placed over the green emitting layer was used to absorb green light and re-emit in the red visible spectrum (peak wavelength 607 nm). Thereby Leising *et al.* achieved 90 % quantum efficiency for blue to green conversion and 80 % for blue to red conversion.

In 2002 Duggal *et al.* presented an OLED-device based on the down-conversion concept, which offers illumination quality white light emission [Dugg02]. The white device consisted of a blue light-emitting polymer OLED (performance: current efficiency of 3.03 cd/A, power efficiency of 1.73 lm/W at 5.5 V) and of a series of three down-conversion layers applied on the reverse side of the glass substrate. The layers were comprised of BASF Lumogen F perylene orange in PMMA, BASF Lumogen F perylene red in PMMA and particles of YAG:Ce³⁺ in a poly-dimethyl siloxane silicone matrix. The output spectrum of the resulting white device corresponded to a color temperature of 4130 K on the blackbody locus and a color rendering index of 93. At 5.5 V the white device exhibited a brightness of 1080 cd/m² and a power efficiency of 3.76 lm/W. Duggal *et al.* showed that the use of the down-conversion phosphor system led to an overall power efficiency increase, an effect attributed to the high quantum efficiency of the luminescent converting materials and to the presence of light scattering in the phosphor layer. Using the same down-conversion layer system and a more efficient blue light-emitting polymer OLED (performance: 10 lm/W), Duggal *et al.* presented a 2ft x 2ft large area white OLED panel with a power efficiency of 15 lm/W and a total output of 1200 lm in 2005 [Dugg05]. The white emission corresponded to

CIE-coordinates of $x = 0.36$ and $y = 0.36$ (Color Temperature 4400 K) and a color rendering index of 88.

In 2006 A. Mikami proposed a new structure for down-conversion OLEDs [Mika06]. In this structure an orange emitting color-conversion layer (CCL) was regularly patterned at constant intervals on the substrate. Deep blue light emissive pixels were closely prepared around the CCL dots. The pixels were based on a polymer-small molecule hybrid OLED incorporating a fluorescent blue emitter. The pixel pitch of a unit cell including a blue OLED and a CCL-dot was in the range of 70~300 μm . Thereby the lateral emission from the blue-light emitting layer could be efficiently transferred to CCL by optimizing the lateral propagation of light (SCM – Side-Coupling Color-Conversion Method). In comparison to the sole deep blue emitting OLED, the external quantum efficiency of the white emitting down-conversion device was improved from 5 % to 9 %. The device offered a power efficiency of 9.1 lm/W and its white emission was related to CIE color coordinates $x/y = 0.35 / 0.26$.

Another concept for down-conversion OLED was presented by Li *et al.* in 2007 [Li07]. They demonstrated a novel structure of white sm-LEDs composed of a greenish blue fluorescent emitting layer and a red fluorescent dye-doped hole injection layer of 340 nm thickness. Within the device a part of the greenish blue EL was absorbed by the red fluorescent dye in the thick hole injection layer and converted into red photoluminescence (PL). The whole white emission from the device was a mixture of the greenish blue EL and red PL. The spectrum of the device (CIE $x/y = 0.31 / 0.33$) showed no change at a wide range of current density and during long-term continuous operation. In general, the use of a greenish blue EL component in a down-conversion device offers two remarkable advantages [Krum06a]: First, greenish blue emitting systems are usually more stable than blue emitting systems. Second, in many cases a lower operating voltage can be achieved when comparing a down-conversion device based on blue/green EL to a white emitting device based on a stack incorporating three EL components (RGB vertical stack, see chapter 1.1). This is due to the absence of the red emitting component which often acts as a deep charge carrier trap within the diode.

2.4.C Down-Conversion Model by Duggal *et al.*

A model developed by Duggal *et al.* to describe the generation of white light using down-conversion [Dugg02] is presented in the following. In this model, each down-conversion layer applied on the substrate surface of a blue emitting OLED absorbs a fraction of the input photons and re-emits them at a different wavelength. Thus, the photon-output of the n th down-conversion layer is given by:

$$(Eq. 2-19) \quad S_n(\lambda) = S_{n-1}(\lambda) \exp[-\alpha_n(\lambda)\delta_n] + W_n C_n(\lambda) P_n(\lambda)$$

The first and second term describe the absorption and accordingly the re-emission in layer n . $S_0(\lambda)$ is the output spectrum of the OLED (in photons), $\alpha_n(\lambda)$ is the absorption coefficient of the luminescence converting material in the n th layer, and δ_n is the effective optical path length. The optical path length may differ from the layer thickness due to scattering and non-normal propagation of photons in the down-conversion layer. The re-emission of the luminescence converting material, $P_n(\lambda)$ is normalized (the integral over all wavelengths is unity) and multiplied by a weight factor, W_n , which is given by:

$$(Eq. 2-20) \quad W_n = Q_n \int S_{n-1}(\lambda) \{1 - \exp[-\alpha_n(\lambda)\delta_n]\} d\lambda$$

Here Q_n is the quantum yield of the down-conversion-process and $C_n(\lambda)$ is a self absorption correction, which is given by [Melh61]:

$$(Eq. 2-21) \quad C_n(\lambda) = \frac{\exp[-\alpha_n(\lambda)\delta_n]}{1 - Q_n \int P_n(\lambda) \{1 - \exp[-\alpha_n(\lambda)\delta_n]\} d\lambda}$$

It is assumed that the effective path lengths for the self-absorption process are equal to the effective path lengths for the luminescence process.

Varying the effective absorption lengths of the different down-conversion layers, possible output spectra can be calculated for a given blue light source and given luminescence converting materials.

Furthermore, the model can be used to fit a measured white output spectrum using the effective path lengths and an overall amplitude factor as adjustable parameters. This allows estimating the ratio of white to blue power efficiency, which is given by:

$$(Eq. 2-22) \quad \frac{P_{white}}{P_{blue}} = \frac{\int (S_n(\lambda) / \lambda) d\lambda}{\int (S_0(\lambda) / \lambda) d\lambda}$$

According to the model, the ratio has to be less than one because of the finite quantum yields of the luminescence converting materials and Stokes losses due to the down-conversion process. However, Duggal *et al.* observed an increase in power efficiency from blue to white for their processed devices. They attributed the unpredicted increase in white device efficiency to an increase in light extraction efficiency caused by additional light extraction from substrate wave-guided modes due to light scattering at the YAG:Ce³⁺ particles in the top layer of the device. In chapter 5 this effect will be discussed more in detail.

Another useful magnitude, which can be predicted by the model, is the ratio of blue to white luminous efficiency. Henceforth this ratio is denominated as *conversion factor*, which is given by:

$$(Eq. 2-23) \quad c = \frac{L_{white}}{L_{blue}} = \frac{\int V(\lambda) (S_n(\lambda) / \lambda) d\lambda}{\int V(\lambda) (S_0(\lambda) / \lambda) d\lambda}$$

where $V(\lambda)$ is the sensitivity of the human eye as a function of wavelength. Though light extraction enhancement due to scattering at phosphor particles is not considered here, this ratio can be helpful, when valuating combinations of blue-emitting devices and phosphor materials for the design of white light sources. Due to the sensitivity of the human eye as a function of wavelength this ratio can be higher than 1.

However, this down-conversion model developed by Duggal *et al.* bears evident drawbacks. The model does not allow any predictions about the spectral output as a function of viewing angle due to its one-dimensional character. Furthermore, the model does not offer any predictions about changes in external device efficiency caused by scattering or absorption/isotropic re-emission processes within the down-conversion layers. Finally, the optical path lengths in the model are not linked to the real physical layer thicknesses. In chapter 5 of this work a ray-tracing model of down-conversion OLEDs is proposed, which overcomes these drawbacks.

2.5. Scattering and Absorption by Small Particles

In this section the basic theory of scattering and absorption by small particles is outlined, which is necessary for the understanding of the presented optical investigations of phosphor down-conversion OLEDs in chapter 5. Scattering and absorption by phosphor particles strongly determine the resulting optical properties of down-conversion devices.

2.5.A Interaction between Light and Matter

In classical ray optics and in phenomenological theory (see chapter appendix A) light is treated as a ray-like propagating energy continuum. The focus in corpuscular theory is the interaction of light and matter. Thereby light is considered as electromagnetic radiation. Within one medium the optical properties are characterized by the complex index of refraction and the magnetic permeability μ . Only non-magnetic materials are considered in this work. For non-magnetic materials, the interaction of matter and an electromagnetic wave is not influenced by the magnetic permeability ($\mu = 1$).

The Maxwell equations are the fundament of electrodynamics. They describe the interaction of an electromagnetic field (electric field $\vec{E}$ and magnetic field $\vec{H}$) and matter. The Maxwell equations are given by:

$$(Eq. 2-24) \quad \text{div } \vec{D} = \frac{\vec{\rho}}{\epsilon_0},$$

$$(Eq. 2-25) \quad \text{div } \vec{B} = 0,$$

$$(Eq. 2-26) \quad \text{rot } \vec{E} = -\frac{\partial \vec{B}}{\partial t}, \text{ and}$$

$$(Eq. 2-27) \quad \text{rot } \vec{H} = \frac{\partial \vec{D}}{\partial t} + \vec{J},$$

where $\vec{D}$ is the electric displacement, $\vec{B}$ is the magnetic flux density and $\vec{J}$ is the displacement current density [Jack83].

The Maxwell equations consist of two differential equations for the electric field-vector and the magnetic field-vector respectively. Their combination leads to the universal wave equation of the electric field-vector $\vec{\mathfrak{S}}$:

$$(Eq. 2-28) \quad \Delta \vec{\mathfrak{S}} = \frac{1}{\nu^2} \frac{\partial^2 \vec{\mathfrak{S}}}{\partial t^2},$$

where $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplace-operator and ν is the velocity of propagation.

Now the simple case of a propagating homogeneous transverse wave in a dielectric is considered: The oscillation takes place in the x,y -plane and the propagation is in z -direction. The following solution for the components of the electric field vector can be derived:

$$(Eq. 2-29) \quad \begin{aligned} E_x &= A e^{i\varpi(t - \frac{n}{c}z)}, \\ E_y &= A e^{i\varpi(t - \frac{n}{c}z) + i\delta}, \\ E_z &= 0, \end{aligned}$$

where $\varpi = 2\pi\nu$ is the angular frequency, c is the speed of light in vacuum, A is an amplitude factor, d is a phase constant (if there is a phase shift between E_x and E_y) and $n = c/\nu$ is the refractive index. Here n is a material constant given by the ratio between the speed of light in vacuum and the velocity of propagation in the dielectric. When considering damped waves, n has to be replaced by the complex index of refraction, which is given by

$$(Eq. 2-30) \quad n^* = n + i\kappa,$$

where the absorption coefficient κ is introduced as attenuation constant.

The complex index of refraction can be expressed by the dielectric constant of the corresponding material $\varepsilon = \varepsilon_1 + i\varepsilon_2$:

$$(Eq. 2-31) \quad n = \sqrt{\frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1)},$$

$$(Eq. 2-32) \quad \kappa = \sqrt{\frac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1)},$$

The dielectric constant determines the electric displacement $\vec{D} = \varepsilon_0 \vec{\varepsilon} \vec{E}$ in the material due to an electric field $\vec{E}$ (ε_0 : electric permittivity of free space). If the material is non-absorbing ε_2 is zero. If the material is absorbing energy, the displacement $\vec{D}$ cannot follow the variations in the electric field $\vec{E}$. In this case the imaginary part of the dielectric constant ε_2 is >0 .

ε_1 and ε_2 are coupled and the functional dependence between them is given by the Kramers-Kronig integrals [Shei05]:

$$(Eq. 2-33) \quad \varepsilon_1(\omega) = 1 + \frac{2}{\pi} \wp \int_0^\infty \frac{\varepsilon_2(\omega') \omega'}{\omega'^2 - \omega^2} d\omega',$$

$$(Eq. 2-34) \quad \varepsilon_2(\omega) = -\frac{2\omega}{\pi} \wp \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega',$$

where $\wp$ is the Cauchy principle value of the integrals [Kowa94]. Eqs. 2-33 and 2-34 show that light dispersion and absorption processes are coupled. They have the same physical basis as that of the excitation and relaxation processes of the electrical dipoles in the medium.

Despite the well-developed theory of light interaction with matter, in practice empirical models are preferred. For example, in wavelength regions, where the materials are transparent or weakly absorbing ($\varepsilon_2 \approx 0$), the Cauchy approximation is often applied [Tomp99]:

$$(Eq. 2-35) \quad \varepsilon_{1C}(\lambda) = A_C + \frac{B_C}{\lambda^2} + \frac{C_C}{\lambda^4},$$

A_C , B_C and C_C are model constants and λ the wavelength. Usually, A_C and B_C have positive values and in most cases C_C can be neglected [Tomp99]. In the spectral region of absorption one or more Lorentz shaped peaks are added to the Cauchy expression:

$$(Eq. 2-36) \quad \varepsilon_1(\lambda) = \varepsilon_{1C} + \sum_i \frac{A_L \lambda^2 (\lambda^2 - L_L^2)}{(\lambda^2 - L_L^2)^2 + \Gamma_L^2 \lambda^2},$$

$$(Eq. 2-37) \quad \varepsilon_2(\lambda) = 0 + \sum_i \frac{A_L \lambda^3 \Gamma_L}{(\lambda^2 - L_L^2)^2 + \Gamma_L^2 \lambda^2},$$

where A_L , L_L and Γ_L are amplitudes, center wavelengths and the full width at half maximum for the i -th peak respectively. Eqs. 2-36 and 2-37 can be derived by using the classical oscillator harmonic oscillator approximation for the dipole transitions determining the relevant optical properties of the material.

2.5.B Description of Scattering and Absorption according to MIE-Theory

The interaction of an electromagnetic wave with matter leads to polarisation and a response of the matter. This can be a process such as scattering or absorption of the wave of incidence. For the description of this interaction a mathematical representation considering the properties of matter is needed.

Mie-theory, also called Lorenz-Mie theory⁴, is a complete analytical solution of Maxwell's equations for scattering and absorption of electromagnetic radiation by spherical particles (also called Mie scattering).

The incidence of an electromagnetic plane wave onto a dielectric sphere is considered in this model [Mie08]. Analysis of the universal wave equation shows that electromagnetic oscillations are initiated within the sphere. The sphere acts as an oscillating multi-pole and thus, acts as the emission center of new waves, which interfere. Initially the wave equation including the Laplace operator is arranged, after the time function has been separated as a harmonic oscillation. Here the polar coordinates r, φ, ϑ are used, which are the appropriate choice in the consideration of a radial symmetric system like a sphere. The solution of the universal wave equation can be found in the references [Bohr83], [Huls57]. It can be expressed as a sum product of three complex functions. For example, the solution for the radial component of the electric field-vector $\vec{\mathfrak{E}}$ is given by

⁴ Lorenz-Mie theory is named after its developers, German physicist Gustav Mie and Danish physicist Ludwig Valentine Lorenz, who independently developed the theory of electromagnetic plane wave scattering by a dielectric sphere in 1908.

$$(Eq. 2-38) \quad E_r = \sum_{j=1}^{\infty} A_j(n, \alpha) \Theta_j(\mathcal{G}) \Phi(\varphi),$$

where n is the complex refractive index, and

$$(Eq. 2-39) \quad \alpha = \frac{D\pi n_0}{\lambda}.$$

Here D is the sphere diameter and n_0 the refractive index of the surrounding medium. In particular, the complex functions stand for:

$A(n, \alpha)$	spheric Bessel function
$\Theta(\mathcal{G})$	sphere function (spheric Legendre polynomials)
$\Phi(\varphi)$	exponential function

The summation describes the superposition of the initiated partial oscillations.

The absolute squares of the electric field-vector $\mathfrak{E}$ are formed in order to obtain the intensities, which results in two expressions $I_{\parallel}$ and $I_{\perp}$, one for the intensity parallel and one for the intensity normal to the plane of incidence. Due to axial symmetry, $I_{\parallel}$ and $I_{\perp}$ are only a function of $\mathcal{G}$ for given sphere parameters n and α .

The solution of the Mie-theory shows that in the case of small spheres the whole sphere oscillates as a single dipole. The oscillation takes place symmetrically to the direction of wave incidence. Additional oscillations of multipoles occur, considering larger spheres. These secondary oscillations are not in phase. In Fig. 2-12 the superposition of all partial waves is plotted for the case of spherical rutile ($n = 2.6$) particles of diameter $D = 0.5 \mu\text{m}$, $1 \mu\text{m}$ and $3 \mu\text{m}$ surrounded by a medium of refractive index $n_0 = 1.5$. With increasing particle size the superposition of the partial waves leads to a more and more complex spatial distribution with an increasing number of maxima and minima. Thereby the fraction of radiation scattered to the backward half-space decreases in comparison to the fraction of radiation scattered into the front half-space. The spatial distribution as a function of $\mathcal{G}$, which results from the superposition of all partial waves, is called the *scattering function*.

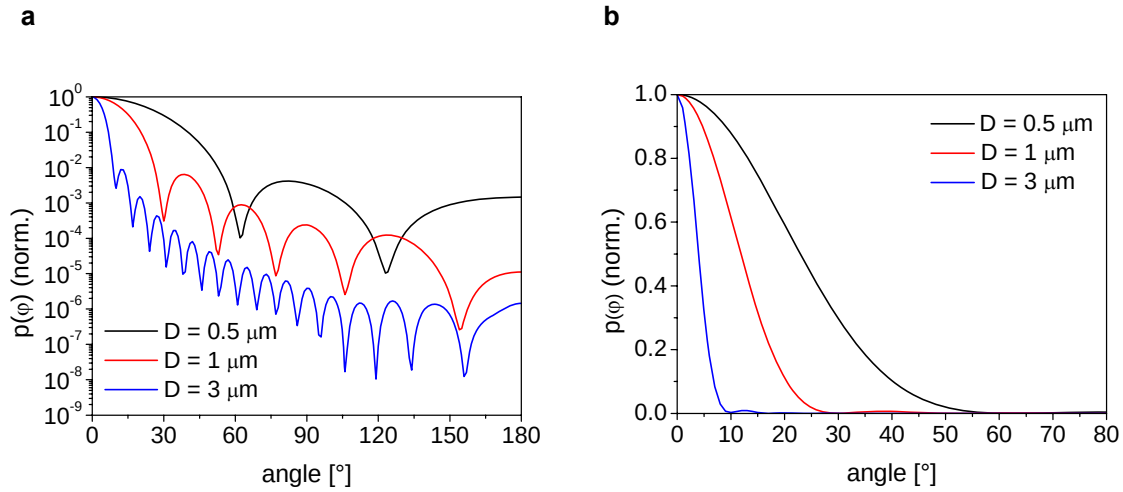


Fig. 2-12. Logarithmic plot (a) and linear plot (b) of the scattering function for the case of spherical rutile ($n = 2.6$) particles of diameter $D = 0.5 \mu\text{m}$, $1 \mu\text{m}$ and $3 \mu\text{m}$ surrounded by a medium of refractive index $n_0 = 1.5$ ($\lambda = 550 \text{ nm}$). The angle of 0° corresponds to the direction of wave incidence.

The *scattering cross section* and the *absorption cross section* can be derived from the solutions $I_{\parallel}$ and $I_{\perp}$. Therefore the fractions of $I_{\parallel}$ and $I_{\perp}$, which are absorbed in the sphere, and the corresponding fractions scattered into the surrounding space are summed up. This is achieved by forming the integral over the unit sphere in relation to the sphere cross section $D^2 \pi / 4$:

$$\begin{aligned}
 \text{(Eq. 2-40)} \quad Q &= \frac{1}{D^2 \pi} \cdot \frac{1}{4\pi} \int_{\varphi=0}^{2\pi} d\varphi \int_{\vartheta=0}^{\pi} f(\vartheta) (I_{\parallel} + I_{\perp}) \sin \vartheta d\vartheta \\
 &= \frac{2}{D^2 \pi} \int_0^{\pi} f(\vartheta) (I_{\parallel}(n^*, \alpha, \vartheta) + I_{\perp}(n^*, \alpha, \vartheta)) \sin \vartheta d\vartheta
 \end{aligned}$$

with $f_s = \frac{3}{8}(1 - \cos \vartheta)$ for scattering, and $f_A = 2$ for absorption.

The integral leads to two magnitudes: the scattering cross section Q_S (real part of Q) and the absorption cross section Q_A (imaginary part of Q). Q_A and Q_S are the ratios between the optically effective cross section to the geometric cross section q_{geo} .

$$(Eq. 2-41) \quad Q_A(n^*, \alpha) = \frac{q_{opt}}{q_{geo}} = \frac{q_A}{\frac{D^2 \pi}{4}},$$

$$Q_s(n, \alpha) = \frac{q_s}{\frac{D^2 \pi}{4}}.$$

The volume specific magnitudes are obtained by the division of q_a and q_s respectively by the sphere volume:

$$(Eq. 2-42) \quad k_1(\lambda, n, \kappa, D) = \frac{q_A}{V} = \frac{3}{2D} Q_A(n^*, \alpha),$$

$$s_1(\lambda, n, D) = \frac{3}{2D} Q_s(n, \alpha).$$

For a collective of monodisperse spheres the ratios Q_s/α and Q_A/α are proportional to the scattering and absorption coefficient respectively. However, a polydisperse particle size distribution is given in case of a phosphor powder. Here the summation of the corresponding fractions weighted by the volume-based particle size distribution $\nu_V(D)$ leads to the representing values k and s :

$$(Eq. 2-43) \quad k(\lambda, n, \kappa) = \int_0^\infty \nu_V(D) k_1(\lambda, n, \kappa, D) dD,$$

$$s(\lambda, n) = \int_0^\infty \nu_V(D) s_1(\lambda, n, D) dD.$$

These volume specific magnitudes k and s are proportional to the absorption coefficient K and the scatterance S given in the Kubelka-Munk equation (see appendix A).

Contemplating a luminescence converting layer, where phosphor particles are embedded in a transparent matrix material, photons propagating in the matrix are scattered or absorbed by the particles. Considering the impingements of photons at the particles, the

average scattering cross section $\bar{q}_s(\lambda)$ and the average absorption cross section $\bar{q}_A(\lambda)$ are determined by:

$$(Eq. 2-44) \quad \bar{q}_s(\lambda) = \frac{\int_0^{\infty} \nu(D) \cdot q_s(\lambda, D) dD}{\int_0^{\infty} \nu(D) dD},$$

$$\bar{q}_A(\lambda) = \frac{\int_0^{\infty} \nu(D) \cdot q_A(\lambda, D) dD}{\int_0^{\infty} \nu(D) dD},$$

where $q_s(D)$ and $q_A(D)$ are given by Eq. 2-41, and $\nu(D)$ is the frequency distribution of phosphor particle size. Accordingly, the average scattering function $\bar{p}(\vartheta, \lambda)$ is formed based on the variety of scattering functions $p_D(\vartheta, \lambda)$ related to the particles of different size D :

$$(Eq. 2-45) \quad \bar{p}(\vartheta, \lambda) = \frac{\int_0^{\infty} \nu(D) \cdot p_D(\vartheta, D) dD}{\int_0^{\infty} \nu(D) dD}.$$

The average scattering cross section, the average absorption cross section, and the average scattering function form the *average single scattering/absorption characteristics*, which describe the average behaviour of a photon impinging a phosphor particle in the phosphor layer of a down-conversion OLED.

3. The Blue Light Source

The resultant efficiency of a white light emitting down-conversion OLED device is mainly determined by the efficiency of the underlying blue OLED. Highly efficient solution processed blue electrophosphorescent organic light-emitting diodes (PHOLEDs) are presented in this chapter. A phosphorescent dye and a non-conjugated polymer host, molecularly doped with electron transporting molecules are utilized. Blue PHOLEDs with power efficiency of 14 lm/W at a current efficiency reaching 22 cd/A, based on a bilayer device architecture, are demonstrated. The results show that simple solution processed devices can have efficiencies similar to those published to date for small molecule multilayer PHOLEDs, based on the same emitter. Analysis of device performance indicates that this high efficiency is achieved by a combination of improved charge balance and light outcoupling efficiency. Changes in the electroluminescent spectra for the device series indicate the presence of optical half-micro cavity effects, which are quantified by means of optical simulation. Furthermore, this allows factoring out the contribution of half-micro cavity effects on device efficiency, enabling the quantification of the charge balance effect on device performance. Before demonstrating the own results, a brief survey of previous work on blue OLEDs is given.

3.1. State of the Art of Blue OLEDs

The generation of white light by the means of down-conversion is based on a blue emitting light source. In OLED-technology blue continues to be the most difficult portion of the spectrum for which to find efficient systems and it is critical to the development of white light sources. In general, blue-emitting light sources have lower photometric efficiencies than green devices due to the lower sensitivity of the human eye in the blue spectral range (see chapter 2.3). Furthermore, the large band gap energy of blue emission may block injection of charge carriers into the light-emitting layer, which leads to reduced efficiency. Another challenging task in this field is the development of suitable large band gap host materials (see chapter 2.1 B) for blue-emitting dyes. The state of the art of blue OLEDs based on the three most common device-concepts is reviewed (also see Table 3-1) in the following. These

concepts are in particular devices comprising conjugated polymer materials, devices comprising small molecule materials including a fluorescent emitter and devices comprising small molecule materials including a phosphorescent emitter.

Polymer light-emitting diodes (PLEDs) have attracted much attention as an accessible flat panel display device and have shown good progress in the last few years. Many polymers for PLEDs have been reported since 1990 [Burr90], [Naka91], [Brau91], [Ohmo91], [Grem92], [Doi93], [Gree93]. Among various blue-emitting materials reported, oligophenyls with spirobifluorene as a central linkage are prominent for simultaneously owning relatively high morphological stability and luminescence efficiency in thin films [Steu00], [Salb97]. The tetrahedral bonding at the spiro center imposes a perpendicular relationship between the two connected oligophenyl chromophores that determine the electronic and optical properties of the compound. Such a steric non-planar structure hinders close packing and interaction between chromophores, the molecules having less subject to crystallization and luminescence quenching in thin films, which leads to an improvement in efficiency. Devices having a power efficiency of ~ 5 lm/W and a lifetime of over 1000 h at a brightness of 100 cd/m^2 have been developed using spirobifluorenes and polyfluorenes [Boli03], [Liu06]. Blue PLED displays find their first applications in commercial products [Phil03].

Stable blue emitting devices based on fluorescent molecular materials have been reported, which typically are based on 2,2',7,7'-tetrakis(2,2-diphenylvinyl)-spiro-9,9'-bifluorene (DPVBi) [Vest01], Spiro-Anthracene [Gebe05] or 4,4'-bis-(N,N-diphenylamino)-quaterphenyl (4TPD) [Gebe05]. The efficiencies of such devices are in the same magnitude as the efficiencies reported for blue PLEDs. Kim *et al.* presented blue small molecule OLEDs (sm-LEDs) with a lifetime of 30000 h at a brightness of 100 cd/m^2 [Kim04]. More and more commercial products such as MP3-players, cell phones, portable DVD-players or digital cameras are equipped with blue or full color displays based on sm-LEDs.

Efficient charge injection at interfaces and low ohmic losses in the transport layers are key factors to obtain high power efficiency and low operating voltages. These requirements are very well fulfilled in conventional light-emitting diodes from inorganic semiconductors by using heavily n- and p-doped electron and hole transport layers, leading to efficient tunneling injection and flat-band conditions under operation. In contrast, organic devices still need comparatively high operating voltages. These device concepts from inorganic devices can be generalized to organic sm-LEDs when developing multi layer systems [Gebe05], [Huan02], [He04]. Highly efficient p-i-n type blue OLEDs with a doped hole injection and transport layer and with a doped electron transport layer show remarkably

improved properties. Due to an increased conductivity of organic semiconducting layers by doping with either electron donors (for electron transport materials) or electron acceptors (for hole transport materials), the voltage drop across these films can be significantly reduced. Such p-i-n type device structures guarantee an efficient carrier injection from both side contact electrodes into the doped transport layers, and low ohmic losses in these highly conductive layers.

A major contribution to efficiency improvement can be the application of heavy metal-complexes as light-emitting dyes, where spin-orbit coupling leads to singlet-triplet state mixing, resulting in high-efficiency electrophosphorescence (see chapter 2.1 B). This has enabled the fabrication of green emitting PHOLEDs with external quantum efficiencies approaching 20% and power efficiency in the order of 70-80 lm/W [Adac01b], [Ikai01]. When using an appropriate choice of phosphorescent dye dopants diluted in a host material with wide energy gap, blue electrophosphorescence can be generated by energy transfer from the host to the phosphorescent guest molecule. However, to make sure that the preferred sites for triplet excitons are on the dopants, the triplet gap of the host should be larger than that of the guest. In the opposite situation, where triplet transfer from the host to the guest is endothermic, the effective lifetime of the triplets in the emission layer is increased, which favors nonlinear quenching processes such as triplet-triplet-annihilation. This requirement becomes more and more difficult to fulfill with deeper blue guest dyes. The highest efficiencies reported for blue PHOLEDs are based on devices fabricated with multiple organic layers comprised of small molecule materials which are prepared by thermal vapor deposition under high vacuum. Blue devices with a power efficiency of 14 lm/W and external quantum efficiency of 12 % have been reported in the recent past, based on small molecule materials [Holm03a]. In particular, for the case of the blue phosphorescent emitter Iridium (III)bis[(4,6-di-fluorophenyl)-pyridinato-N,C²]picolate (FIrpic), Tokito *et al.* have reported devices with efficiencies of 20.4 cd/A and 10.5 lm/W [Toki05]. However, the utilization of multiple layers in such small molecule devices are expected to result in considerably more complex device fabrication methodology, leading to higher fabrication costs. To utilize OLEDs for low-cost general lighting applications, a simple solution based processing approach is desirable, provided the efficiency of devices is not compromised.

Table 3-1. Survey over efficient blue OLEDs representing the state of the art: (a) blue OLEDs based on polymeric emitters, (b) blue OLEDs based on fluorescent small molecular emitters, (c) blue phosphorescent OLEDs processed by evaporation. The emitter materials are printed in bold letters. The peak wavelength of the EL-spectrum or the CIE color coordinates in brackets are given in the column “color”.

a)

device	efficiency	color	additional information	reference
blue emitting polymer	>3 cd/A, $\eta_{\text{ext}} = 2.3\%$	(.17/.21)	1000 h lifetime DC at 300 cd/m ²	[Boli03]
ITO/PEDOT/ poly(arylene viylene) /LiF/Al	1.2 cd/A	440, 464 nm (.15/.10)		[Doi03]
ITO/PEDOT/ poly(arylene viylene) /LiF/Al	2.2 cd/A	460 nm, (.16/.20)		[Doi03]

b)

device	efficiency	color	additional information	reference
ITO/TPD/ MPS / Alq ₃ /LiF/Al	14 lm/W at 5 cd/m ² , 20 cd/A, $\eta_{\text{ext}} = 8\%$	490 nm		[Chen02]
ITO/NPB/ TSB / Alq ₃ /LiF/Al	1.57 cd/A at 6V	464 nm, (.19/.23)	max. brightness: 1663 cd/m ² at 14 V	[Chen04]
ITO/NPB/ TBVB / Alq ₃ /LiF/Al	1.62 cd/A at 5 V	468 nm, (.20/.26)	max. brightness: 2154 cd/m ² at 14 V	[Chen04]
ITO/Meo-TPD: F ₄ -TCNQ/ Spiro-TAD/ spiro-anthracen / TAZ/Bphen:Cs/Al	4.5 cd/A, $\eta_{\text{ext}} = 3\%$	(.14/.14)		[Gebe05]
ITO/Meo-TPD: F ₄ -TCNQ/ Spiro-TAD/ 4P-TPD /TAZ/ Bphen:Cs/Al	1.3 lm/W, 1.6 cd/A, $\eta_{\text{ext}} = 2.4\%$	(.15/.09)		[Gebe05]

ITO/ MTDATA/ NPB/CuPc/ NPB / BCP/Alq ₃ /Al	2.62 cd/A	(.18/.16)	max. brightness: 6942 cd/m ²	[Jian05]
ITO/2- TNATA/NPB/ LiPBO doped BDP VPA/Alq ₃ / LiF/Al	2.9 lm/W at 160 cd/m ² , 25 cd/A	(.16/.15)	L lifetime: 20000 h AC at 150 cd/m ² , 30000 h AC at 100 cd/m ²	[Kim04]
ITO/PEDOT/ PVK/ BDP Q/ LiF/Al	3.33 cd/A, at 100 cd/m ² , $\eta_{\text{ext}} = 4.1\%$	453 nm (.15/.12)	max. brightness: 925 cd/m ²	[Kulk05]
ITO/CF _x /c- HTL/NPB/5% BD1 in MADN/ Alq ₃ /LiF/Al	2.5 lm/W, 5.4 cd/A, $\eta_{\text{ext}} = 5.1\%$	(.14/.13)	1080 cd/m ² at 6.8V	[Lee05]
ITO/NPB/ DNA / TPBI/ Alq ₃ /LiF/MgAg	3.6 cd/A	(.145/.145)	680 cd/m ² at 20 mA/cm ² and 5.5 V	[Lio02]
ITO/TPD/ LiOXD /Al	1.1 lm/W, 3.9 cd/A	468 nm		[Lian03]
ITO/CF _x /c-HTL (CuPc,NPB)/ NPB/ DAS-Ph doped MADN/Alq ₃ / LiF/Al	7.9 lm/W, 16.2 cd/A at 3229 cd/m ² , $\eta_{\text{ext}} = 8.7\%$	(.15/.29)		[Liao05]
ITO/ TPD /BCP/ LiF/Al	0.5 lm/W, $\eta_{\text{ext}} = 0.5\%$	466 nm	max. brightness: 2010 cd/m ²	[Qiu04]
ITO/TPD/ DPVBi /LiF/Al	$\eta_{\text{ext}} = 1.4\%$	476 nm	max. brightness: 3000 cd/m ² at 12 V	[Shah98]
ITO/CuPc/ NPB/ a perylene doped aluminum chelate/Alq ₃ / MgAg	2 cd/A	492 nm, (.161/.215)	1100 h lifetime at 337 cd/m ² under 1 kHz AC (average $j = 20$ mA/cm ²)	[Slyk96]
ITO/CuPc/ DPF / Alq ₃ /Mg:Ag	3.0 lm/W, 5.3 cd/A	(.16/.22)		[Tao05]

ITO/PEDOT/ NPB/CBP/ 6% TPF doped DPF/BCP/Ca/ Al	3.33 cd/A, $\eta_{\text{ext}} = 2.4\%$	456 nm, (.164/.188)	max. brightness: 6210 cd/m ² at 269 mA/cm ²	[Tsen06]
ITO/PANI/ MTDATA/ Spiro-TAD spiro-DPVB i/ Alq ₃ /cathode	4 cd/A	467 nm	100 cd/m ² at 5 V, 1000 cd/m ² at 6 V, 10000 cd/m ² at 8 V	[Vest01]
ITO/PEDOT/ NCB/ TBPSF / Alq ₃ /LiF/Al	1.6 cd/A	440 nm	max. brightness: 30 000 cd/m ²	[Wu02]
ITO/PEDOT/ NCB/ TBPSF , perylene doped , Alq ₃ / LiF/Al	5.2 cd/A	460, 480 nm	max. brightness: 80 000 cd/m ²	[Wu02]
ITO/TPD/ CBP: BCzVB / Alq ₃ /LiF/Al	3.5 cd/A, $\eta_{\text{ext}} = 2.6\%$	(.15/.16)	max. brightness: 8500 cd/m ²	[Wu04]
<i>c)</i>				
device	efficiency	color	additional information	reference
ITO/CuPc/ NPB/ FIrpic in CBP/BAlq/LiF/ Al	6.3 lm/W, $\eta_{\text{ext}} = 5.7\%$	475 nm, (.16/.29)		[Adac01a]
ITO/CuPc NPB/6% FIrpic in mCP/ BAlq/LiF/Al	8.9 lm/W, $\eta_{\text{ext}} = 7.5\%$		max. brightness: 9500 cd/m ² @ 100 mA/cm ²	[Holm03b]
ITO/NPD/mCP/ FIr6 in UGH2 /BCP/LiF/Al	13.9 lm/W, $\eta_{\text{ext}} = 11.6\%$	(.16/.26)	11800 cd/m ² @ 156 mA/cm ²	[Holm03a]
ITO/NPB/TCTA/ m-Ir(pmb) ₃ in UGH2/BCP/ LiF/Al	5.8 cd/A, 1.7 lm/W	(.17/.06)		[Holm05]

3.2. Highly Efficient Solution Processed Blue Organic Electrophosphorescent Diodes

Blue PHOLEDs based on a simple bilayer structure are reported in this section [Krum06c], [Math06]. In this case, the light-emitting polymer layer (LEP) is formulated on the basis of a non-conjugated polymer into which electron transporting moieties and a phosphorescent blue emitter are dispersed in suitable proportions. This is a typical molecularly doped system which has been extensively studied in the past years and successfully implemented in green and blue solution processed PHOLEDs [Yang04a], [NakaA04]. These devices incorporate some of the best features of both small molecule and polymer devices: The high degree of electronic variability of the small molecule building blocks is combined with the ease of fabrication of PLEDs. Moreover, the high triplet energies available in small molecules can be replicated using non-conjugated polymers (e.g. polyvinylcarbazole, PVK) as a host matrix. PVK is one of the most commonly used polymers in molecular doped PLEDs due to its excellent film-forming properties, high glass transition temperature, wide energy gap and good hole mobility of $\sim 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at electric fields typical for OLED operation (10^6 Vcm^{-1}) [Gill72].

Variation in the composition of the LEP of the presented devices indicates that two factors are responsible for differences in device efficiency. One of the factors is the charge (electron and hole) balance in the device. The other is the location of the exciton density profile within the LEP, which affects the light outcoupling from the device. The devices optimized for both factors have a power efficiency of 14 lm/W and a current efficiency of 22 cd/A. This implies that solution processed devices can have as high an efficiency as small molecule multilayer blue PHOLEDs in spite of their simple bilayer device architecture, which is an important requirement in order to develop cost-effective solutions for the application of OLEDs in general lighting.

3.2.A Device Structure

Fig.3-1 shows the structure of the devices used in this study. Each substrate has 4 individual OLEDs with a 0.4 cm^2 active area. The LEP is comprised of PVK as the hole transporting matrix, 1,3,4-oxadiazole,2,2'-(1,3-phenylene)bis(5-(4-(1,1-dimethylethyl)phenyl)) (or OXD-7) as an electron transporter and the blue phosphorescent dye Iridium (III)bis[(4,6-di-fluorophenyl)-pyridinato-N,C²]picolinate (FIrpic) (HOMO and LUMO values and

chemical structures of PVK and Flrpic are given in Fig. 3-2). Keeping the amount of Flrpic in the LEP constant at 10% by weight, the relative concentrations of PVK and OXD-7 are changed in order to vary the hole and electron transport within the LEP. The OLEDs are fabricated as follows. A thin (60 nm) film of PEDOT:PSS was spin-coated atop the ITO and then baked for 30 min at 200 °C on a hot plate. The LEP is deposited atop PEDOT:PSS, followed by thermal evaporation of the cathode layers comprising CsF and Al. The LEP (thickness of 75nm) is spin-coated from chlorobenzene and is baked at 80 °C for 30 min on a hot plate. Device characterization is carried out after encapsulating the OLEDs.

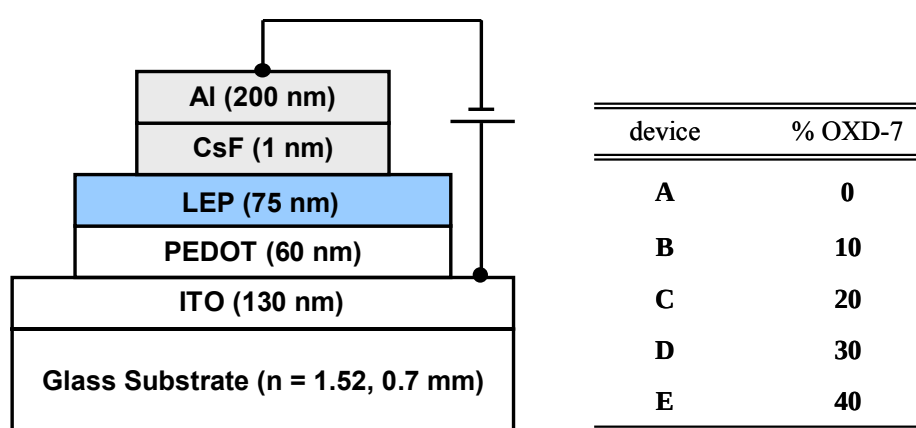


Fig. 3-1. Architecture of the devices used in this study. The table contains the device nomenclature based on the composition of the LEP.

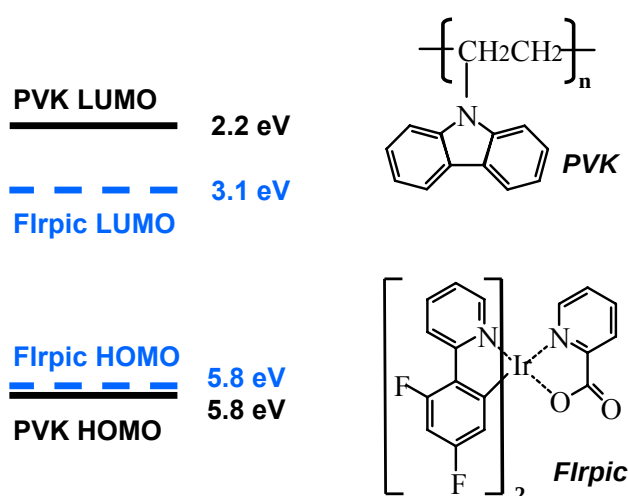


Fig. 3-2. Chemical structures and HOMO/LUMO levels of PVK and Flrpic [Daub99], [Yang04b], [Broo04].

3.2.B Influence of Charge Balance on Resultant Device Efficiency

To get a first understanding of the device performance with varying OXD-7 concentration, the current density-voltage (J-V) characteristics of the devices used in this study were measured by means of a Keithley 238 as current source and a Keithley 6514 as voltmeter (Fig. 3-3). For comparison, the J-V data for a device with identical charge injecting electrodes, where the LEP is comprised of neat PVK (henceforth referred to as the PVK device), was also measured. Compared to the other devices, device A with only FIrpic and no OXD-7 in the LEP has a very low current density. The slope of the J-V characteristics becomes steeper with increasing OXD-7 concentration. The J-V characteristic corresponding to the PVK device shows the steepest slope, i.e. the PVK device shows the highest conductivity.

Compared to the PVK device, device A with only FIrpic and no OXD-7 in the LEP has a very low current density. The values reported for the HOMO and LUMO values of PVK and FIrpic are considered in order to explain this. The HOMO values reported for PVK and FIrpic are relatively close to each other [Daub99], [Yang04b], [Broo04] and hence it is not possible, based on literature, to determine whether there is trapping of holes by the inclusion of FIrpic. At the same time, based on the LUMO values reported for PVK (2.2 eV) [Yang04b] and FIrpic (3.1 eV) [Broo04], it appears that FIrpic may be acting as a deep electron trap in the PVK device.

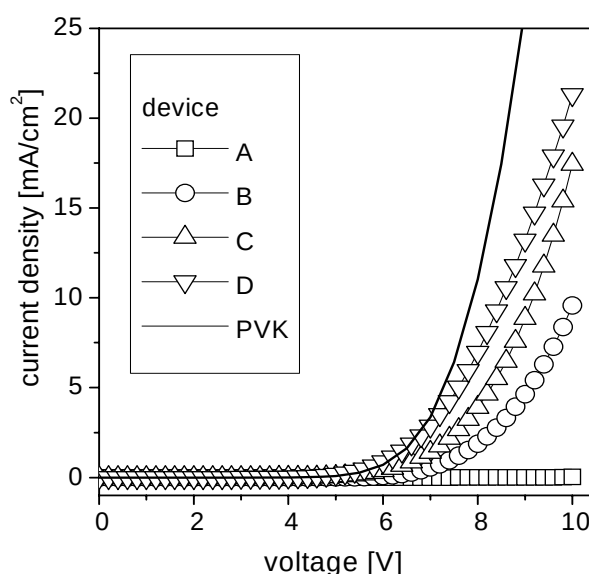


Fig. 3-3. Variation in current density vs. voltage for the devices used in this study.

It is important to note, however, that the measured electron mobility of neat FIrpic is comparable to that of the commonly used electron transport material in OLEDs, viz, Aluminum tris(8-hydroxyquinoline) (Alq_3) [Mats05], and hence the main factor causing trapping of electrons by FIrpic may be the concentration of FIrpic in the LEP, which is less than the percolation regime, where electrons are expected to be transported by hopping between FIrpic molecules alone.

The introduction of OXD-7 as an electron transporting moiety into the LEP for devices B-D results in an immediate rise in current density at any given voltage (Fig. 3-3), which increases with increasing OXD-7 concentration. The rise in current density is most likely due to better electron transport within the LEP assisted by the presence of OXD-7 in the LEP. For all devices, the EL-spectra are seen to be entirely due to FIrpic emission with CIE-coordinates of $x = 0.17$, $y = 0.37$ at 1 mA/cm^2 for device D.

In Fig. 3-4, the current efficiency is plotted as a function of current density⁵. Device efficiency is observed to rise with increasing OXD-7 concentration in the LEP between devices A-D. This can be explained as follows. Starting from device A, where hole transport within the LEP is dominant, the charge balance within the LEP is improved with increasing OXD-7 concentration due to better electron transport. The fall in efficiency of device E could be due to too much electron injection into the LEP. The efficiency of device D as a function of brightness is plotted in Fig. 3-5, where peak device efficiencies of 22 cd/A and 14.5 lm/W are obtained at a brightness of 26 cd/m^2 . This compares favourably with published results for similar small molecule devices fabricated by high vacuum thin film coating methodology [Yang04a] and shows the capacity of the chosen approach. Furthermore, the current efficiency of $20\text{-}22 \text{ cd/A}$ is observed to persist up to a luminous intensity as high as 800 cd/m^2 .

⁵ The light output of the devices was measured using a large area ($18 \text{ mm} \times 18 \text{ mm}$) Si photodiode. The distance between the Si photodiode and the OLED substrate's surface was kept at $<0.5 \text{ mm}$. Considering the size of the OLED's active area of 4 mm^2 in comparison to the area of the Si photodiode, this setup offers a nearly entire solid angle collection of the light emitted by the devices. The Si diode was calibrated by measuring the spectral distribution of the devices in the direction normal to the substrate. The emission of the devices was set to be Lambertian. The spectra were measured using a spectral camera Photo Research PR 705.

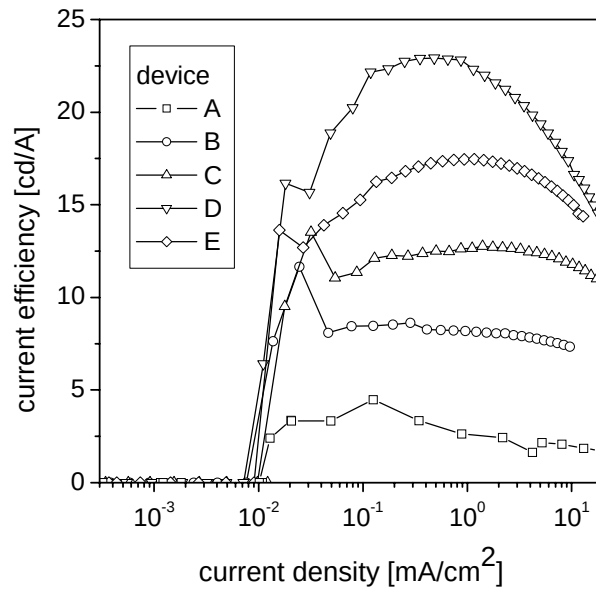


Fig. 3-4. Current efficiency [cd/A] versus current density for devices with varying OXD-7 concentration in the light emitting layer.

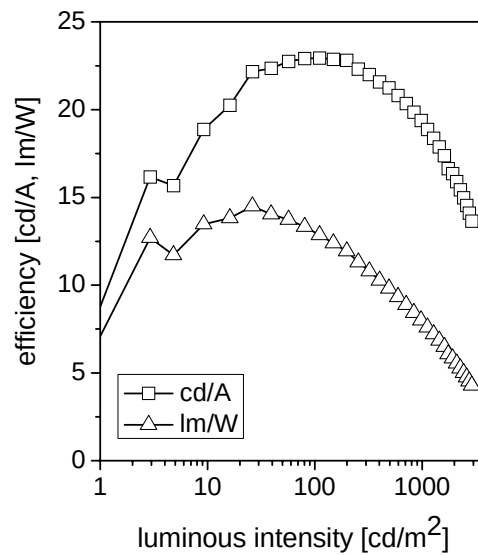


Fig. 3-5. The efficiency of device D as a function of luminous intensity. Peak efficiencies of 22 cd/A and 14.5 lm/W are obtained at a brightness of 26 cd/m².

3.2.C Influence of Optical Half-Micro Cavity Effects on Resultant Device Efficiency

Though in an OLED device the internal device efficiency is highly dependent on the charge balance of the device, at the same time a modification of charge balance could lead to a change in the location of the emission zone (EMZ). This can result in variations in the extent to which light is outcoupled from the device due to the dependence of the optical-half micro cavity effect on the location of the emission zone [Adac01b] (see chapter 2.2). Thus the resultant change in device efficiency is a combined effect of improved charge balance and alterations in the half-micro cavity effect. Improvements in device efficiency are often assigned entirely to charge balance effects without considering half-cavity effects. This is because a general methodology has not been rigorously defined to isolate the relative contribution of both effects on enhancement in device performance. In this section a method is shown which enables the separate quantification of both effects using optical simulation.

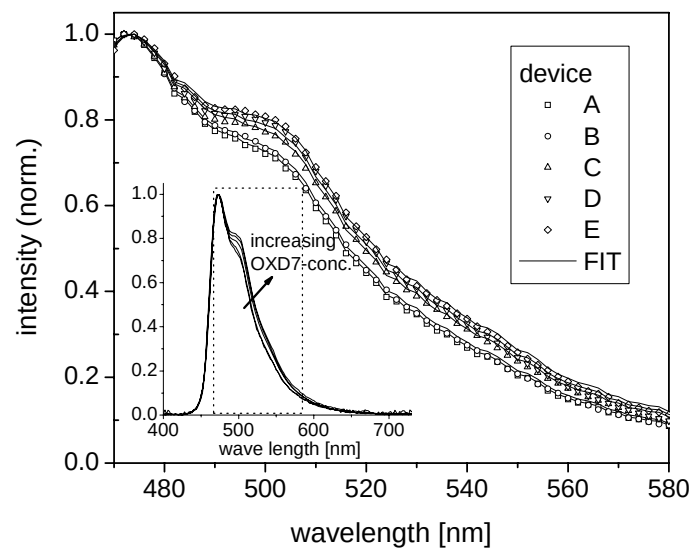


Fig. 3-6. Variation in EL-spectra at a fixed current density of 1 mA/cm^2 for devices with varying OXD-7 concentration. The inset shows the total EL-spectrum for the devices over the entire wavelength range in the visible region.

Fig. 3-6 shows the EL-spectra of the devices A-E, which were measured at a fixed current density of 1 mA/cm^2 in the direction normal to the substrate, using a spectral camera Photo Research PR 705. Considering these spectra, the presence of half-cavity effects can be demonstrated. The inset shows the entire spectrum, while the main portion of the figure is a

magnified portion of the same spectrum in the 500 nm region for all devices. As observed, the shoulder at 500 nm is seen to increase with increasing OXD-7 concentration in the LEP. Thus, at a fixed current density, the spectrum of the FIrpics changes as a function of the OXD-7 content in the LEP. This takes place in spite of the absence of any emission from species other than FIrpics in the LEP.

Changes in the PL-spectra due to the different OXD-7 concentrations were not observed for the devices used in this study (see appendix B). It will be shown that these changes observed in the EL-spectra can be attributed to the variation in the location of the exciton recombination zone within the LEP as its composition is changed.

Using the micro cavity simulation tool described in chapter 2.2, the EL-spectra in the direction of the substrate normal (Fig. 3-6) were fitted. The parameters used for the fit were the location of the EMZ and the internal emission spectrum of the material (EL_0). It is assumed that the photoluminescence spectrum of FIrpics corresponds to EL_0 . The complex index of refraction as a function of wavelength was determined by the means of standard ellipsometry for all organic layers and electrode materials used in this study in order to ensure accurate simulation. The location of the EMZ is needed for the calculation. Here the location of the EMZ is defined as the distance between the cathode and the center of a Gaussian distributed exciton profile within the LEP. In a work published by Wu *et al.* a scope of the exciton distribution of approximately 25 nm was determined experimentally for FIrpics in N,N'-dicarbazolyl-1,4-dimethene-benzene (DCB) [Wu05]. As both PVK and DCB contain carbazole as the functional group, a similar behavior for exciton diffusion is expected. Thus, a full width at half maximum of 20 nm was chosen for the distribution of excitons within the LEP in the simulation. Given the EL-spectrum of each device, the distance between the EMZ and the cathode was varied till the calculated EL_0 matched the photoluminescence PL-spectrum of FIrpics, which is considered to be the actual EL_0 as stated above. According to the simulation results the distance between cathode and EMZ increased from 20 nm for device A to 60 nm for device E. This can be explained as follows: As the amount of OXD-7 in the LEP increases, more electrons are able to penetrate into the LEP. This results in a higher extent of exciton formation in those regions of the LEP which are farther from the cathode.

The effect of the change in the location of the EMZ on device performance due to improved charge balance and optimized location of the EMZ in the optical half-micro cavity is quantified in the following. First, the external light output as a function of the location of the EMZ was determined for the device geometry used in this study (Fig. 3-7). A constant electron-hole balance leading to a uniform recombination rate was assumed in the calculation.

Finally, the contribution of the half-cavity effect to the efficiency improvement is determined by analyzing the external light output. The circles in Fig. 3-7 mark the external light output for the imaginary devices A', B', C', D', E', which all have the same locations of the EMZ as the corresponding real devices A, B, C, D, E. To obtain the actual effect of charge balance, the half-cavity effect is superimposed onto the actual measured experimental data. The portion of the light output not due to half-cavity effects is attributed to the charge balance. This will be illustrated by device A and D.

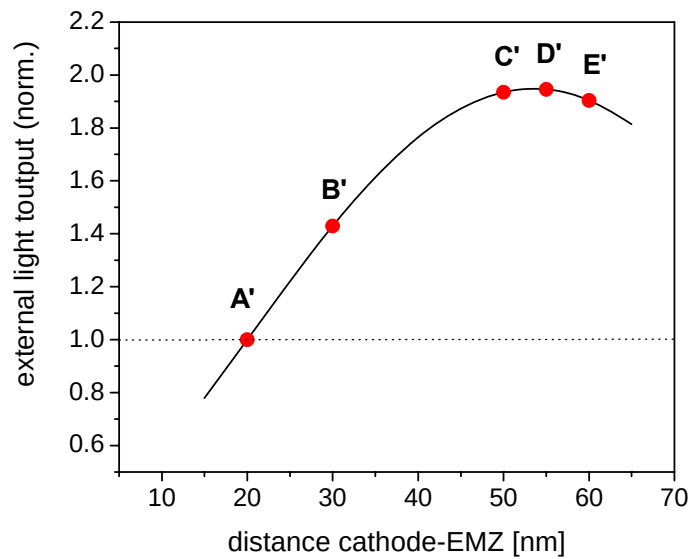


Fig. 3-7. Calculated external light output (for constant current density) as a function of the location of the EMZ. The exciton formation rate was assumed to be constant. The circles in the graph mark the light output for the imaginary devices A', B', C', D', E', which all have the corresponding locations of the EMZ as the real devices A, B, C, D, E. The graph describes the efficiency improvement in comparison to device A due to the optical half-micro cavity effect dependent on the location of the EMZ.

Considering half-cavity effects alone, the light output of device D' is almost twice as high as the output of device A' (Fig. 3-7). However, in the case of the real devices A and D, the light output of device D is 8.5 times higher than that of device A for the same current density (Fig. 3-4). Based on the comparison of devices A' and D', the improvement in device efficiency due to the half-cavity effect is given by the measured output of device D divided by two. The rest of the improvement is due to the effect of improved charge balance.

A more rigorous description of the above calculation can be stated as follows - the improvement due to better charge balance in comparison to device A is given by:

$$(Eq. 3-1) \quad \Delta_1(X) = \frac{O_m(X)}{O(X')} - O_m(A),$$

where $O_m(X)$ ($X \in [B, C, D, E]$) is the measured light output at constant current density and $O(X')$ ($X' \in [B', C', D', E']$) is the light output of the imaginary devices normalized on the output of A'. The improvement compared to device A due to the half-cavity effect is given by:

$$(Eq. 3-2) \quad \Delta_2(X) = O_m(X) - [\Delta_1(X) + O_m(A)] = O_m(X) - \frac{O_m(X)}{O(X')}.$$

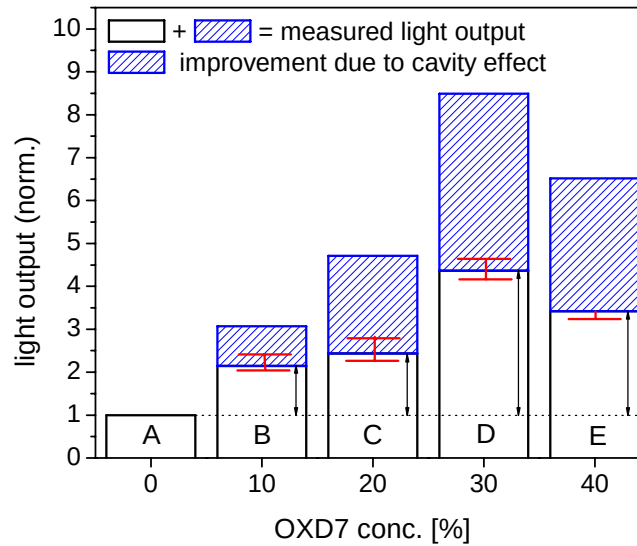


Fig. 3-8. Measured external light output of the devices used in this study. The cross hatched area represents the calculated efficiency improvement compared to device A due to optical half-cavity effects. The improvement in efficiency due to better charge balance is marked by the double ended arrows. The calculation of the error-bars is explained in appendix B.

The block graph in Fig. 3-8 shows the external light output of the devices used in this study (current density of 1 mA/cm^2). The data is normalized on the output of device A. The cross-hatched area represents the efficiency improvement compared to device A due to the half-cavity effect, which has been determined via simulation. The improvement in device efficiency due to better charge balance is marked by the double ended arrows. The effects on

the efficiency due to half-cavity and due to charge balance increase from device A to device D. In comparison to device A the internal efficiency of device D is increased by a factor of 4.4 due to the effect of improved charge balance. The half-cavity effect caused by the change in the location of the EMZ further improves the efficiency by a factor of 1.93 leading to an overall improvement of 8.5 from device A to D. The drop of device efficiency from device D to device E is mainly caused by a decrease in internal device efficiency. This can be attributed to the achievement of optimum charge balance for device D. Additional increase in OXD-7 concentration reduces the light output. This could be a consequence of a tilted charge balance, which might make device E more electron dominant. Additionally quenching effects due to the proximity to the PEDOT layer may have larger contribution.

3.3. Conclusion

In conclusion a simple experimental approach in order to harvest triplets and singlets in organic electrophosphorescent devices has been demonstrated. The use of an uncomplicated, bilayer device architecture has enabled the fabrication of PHOLEDs based on solution processing with performance rivaling those of published multilayer small molecule PHOLEDs. The evolution of device efficiency with different hole-electron balance in the LEP was studied for this class of PHOLEDs. While charge balance was observed to play a major role, optical half-cavity effects also contribute to the improved efficiency. These effects are the result of the movement of the exciton profile within the LEP, and are often not taken into consideration when analyzing the effect of charge balance on device performance. By analyzing the changes in EL-spectra from a series of devices, the location of the EMZ within the LEP can be pinpointed, from which the half-cavity effects can be quantified. Based on this, for the first time a general methodology has been demonstrated, which allows determining the contribution of both charge balance and optical effects while analyzing the performance of devices.

4. Light Extraction Enhancement due to Substrate Surface Modification

An advantageous side effect of a down-conversion layer applied on the substrate surface of a blue OLED can be light extraction enhancement due to scattering by phosphor particles. In general, modifying the light-emitting surface is a well-known approach to increase the external light output of OLEDs. This approach relies on the extraction of light which is wave-guided within the substrate of the unmodified device. Thereby the apparent light extraction enhancement is given by the ratio between the efficiency of the unmodified device and the efficiency of the modified device. This apparent light extraction enhancement is dependent on the OLED architecture itself and is not the correct value to judge the effectiveness of a technique to enhance light outcoupling due to substrate surface modification. In this chapter a general method to evaluate substrate surface modification techniques for light extraction enhancement of OLEDs is proposed, which is independent from the device architecture. The method will be applied in the analysis of light extraction from down-conversion devices in the next chapter. In this chapter the proposed method is experimentally demonstrated using green electrophosphorescent OLEDs with different device architectures. The substrate surface of these OLEDs was modified by applying a prismatic film to increase light outcoupling from the device stack. It was demonstrated that the conventionally measured apparent light extraction enhancement by means of the prismatic film does not reflect the actual performance of the light outcoupling technique. Rather, a more accurate evaluation of light outcoupling enhancement can be achieved by comparing the light extracted out of the prismatic film to that generated in the OLED layers and coupled into the substrate (before the substrate/air interface). Furthermore, it is shown that substrate surface modification can change the output spectrum of a broad band emitting OLED.

4.1. Approaches for Light Extraction Enhancement

One evident drawback of OLEDs is the fact, that only a small amount of generated light is outcoupled. The mismatch of the refractive index between air and the organic layers leads to most of the generated light being lost through total internal reflection into wave-guiding modes and self absorption. As explained in chapter 2.2, the light emitted by a bottom emitting device can be classified into three modes: the external mode, the substrate wave-guided mode and the anode/organic wave-guided mode. Depending on the value of the emission angle with respect to the normal to the substrate, the generated photons are outcoupled or wave-guided into the substrate and the active layers respectively.

Many approaches have been utilized to increase the outcoupling efficiency. These can be divided into six generic schemes: (1) Applying a polymer microlens array on the substrate surface [Peng04], or placing a large size index matching hemispherical lens on top of the substrate [Bulo98]. (2) Introducing scattering effects at the substrate surface by means of techniques such as applying a transparent coating on the substrate with embedded small particles [NakaT04], [Shia04a], [Shia04b], or texturing the substrate surface (for example by sand blasting [Sche01] or sand paper [Lu00]). (3) Incorporating the light-emitting diode in a reflecting mesa structure [Gu97]. (4) Inserting an extremely low refractive index ($n \approx 1.03$) silica aerogel porous layer between the ITO transparent anode and the glass substrate [Tsut01]. (5) Increasing light outcoupling efficiency by means of micro cavity effects due to the double mirror structure of the organic-light emitting device given by both electrodes and the organic layers embedded in between [Jord96]. (6) Application of lateral periodic nano structures on the substrate leading to an increase of light outcoupling through Bragg scattering [Lupt00], [Salt01].

The wave-guided light retained within the substrate of the unmodified device (standard flat glass substrate) is extracted, using the approaches of scheme (1) and (2). The improvement in light outcoupling by various methods of modifying the substrate surface is often quantified by an apparent enhancement factor, $a = \eta_2 : \eta_1$, where η_1 is the external efficiency of the unmodified OLED and η_2 is the external efficiency of the device after modifying the substrate. A strong dependence of the enhancement factor a on the device architecture itself is shown in this chapter. Furthermore, an alternative method to determine the enhancement of light extraction is demonstrated, using light outcoupling approaches of scheme (1) or (2) discussed earlier. The proposed method thus eliminates dependence on

device architecture, which would otherwise lead to inaccurate conclusions regarding the efficiency of the device itself.

4.2. General Method to Evaluate Substrate Surface Modification Techniques for Light Extraction Enhancement

4.2.A Experiment

Fabrication of OLEDs

Fig. 4-1 shows the structure of the green emitting PHOLEDs (peak wavelength 510 nm) used to illustrate the proposed method to evaluate substrate surface modifications. Each substrate has 4 individual diodes with a 0.4 cm^2 active area. The PHOLEDs are fabricated as follows: A thin (60 nm) film of PEDOT:PSS was spin-coated atop the ITO coated substrate and then baked for 30 min at 200°C on a hot plate. The green emitting layer was then spin-coated on the top of the PEDOT:PSS with conditions to yield a light-emitting layer thickness of 70 nm. The LEP was then annealed at 80°C for 30 min. The solution for the LEP consisted of 24 % wt 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), 9% wt 4,4'-bis(m-tolylphenylamino)biphenyl (TPD), 6 % wt fac-tris(2-phenylpyridine)-iridium (Ir(ppy)_3) and of 61 % wt PVK in chlorobenzene [Yang04a]. On top of the LEP a hole-blocking layer consisting of PBD was thermally evaporated in a vacuum coater to a thickness of 10 nm. This was followed by thermal evaporation of a tris(8-hydroxyquinoline)aluminum (Alq_3) layer on top of the PBD layer. Devices with four different values of Alq_3 layer thickness (10 nm, 30 nm, 50 nm, 70 nm) and devices without Alq_3 layer were prepared. Then a CsF layer with a thickness of 1 nm was deposited as an electron injection layer. Finally, an Al layer with a thickness of 200 nm was deposited as the cathode. All the thermally evaporated layers were deposited sequentially in a vacuum coater in a single pump down cycle. All device fabrication steps from the LEP spin-coating to device encapsulation were carried out in an inert nitrogen atmosphere. Three devices were fabricated for each value of Alq_3 layer thickness.

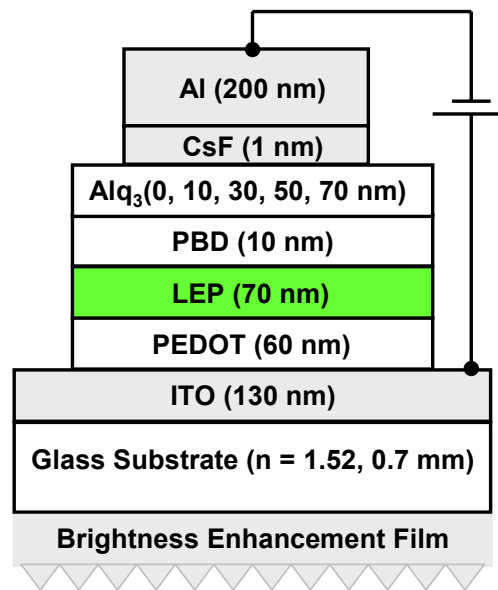


Fig. 4-1. Structure of the PHOLEDs used in this study. Additionally to the standard layout a Brightness Enhancement Film (BEF) was used as light outcoupling enhancement layer.

Brightness Enhancement Film on top of the standard PHOLED

After measuring the light output of the unmodified devices (the method is described in more detail below), a Brightness Enhancement Film (BEF) obtained from 3M (Vikuiti BEF II 90/50) was applied on the surface of the devices. The BEF consists of an acrylic resin with prismatic features on its surface coated on a polyester substrate. The prism angle is 90° and the prism pitch is $50\ \mu\text{m}$ (see Fig. 4-2). The BEF has a nominal thickness of $155\ \mu\text{m}$ and was optically coupled to the glass substrate with optical laminating tape (3M No. 8141, $n = 1.49$). A fraction of the substrate wave-guided light retained within the substrate of the unmodified device is extracted by means of the BEF: Light, which is reflected backwards to the cathode at the interface between BEF and air, is “recycled” (i.e. reflected at the cathode) until it exits at the proper angle or is absorbed in the PHOLED stack.

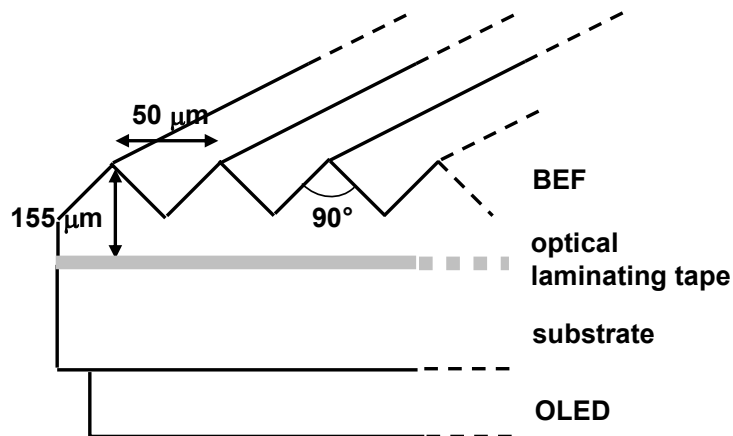


Fig. 4-2. Brightness Enhancement Film (BEF) applied on the substrate surface.

Measurement of Substrate Mode and External Mode Intensity

The PHOLED emission intensity was measured using a large area (18 mm x 18 mm) Si photodiode according to a method described by Nakamura [NakaT04]. The distance between the Si photodiode and the surface of the surface was kept at <0.5 mm (see Fig. 4-3). Considering the size of the PHOLED's active area in comparison to the area of the Si photodiode, this setup offers a nearly entire solid angle collection of the light emitted by the devices. Measurements were carried out alternatively with an air gap and an optical gel obtained by Norland (NOA 63), whose refractive index was 1.56. When the air gap was filled with gel, total internal reflection at the glass/air interface disappeared, enabling the emitted light of the external and substrate wave-guided modes to be measured by the Si photodiode simultaneously. Thus three intensities I_{air} , I_{gel} and I_{film} were measured, where I_{air} and I_{gel} were the emission intensity detected by the Si photodiode at the air and gel gaps before modifying the device, and where I_{film} was the emission intensity detected at the air gap after applying the BEF. All intensities were measured at a constant current density of 1 mA/cm².

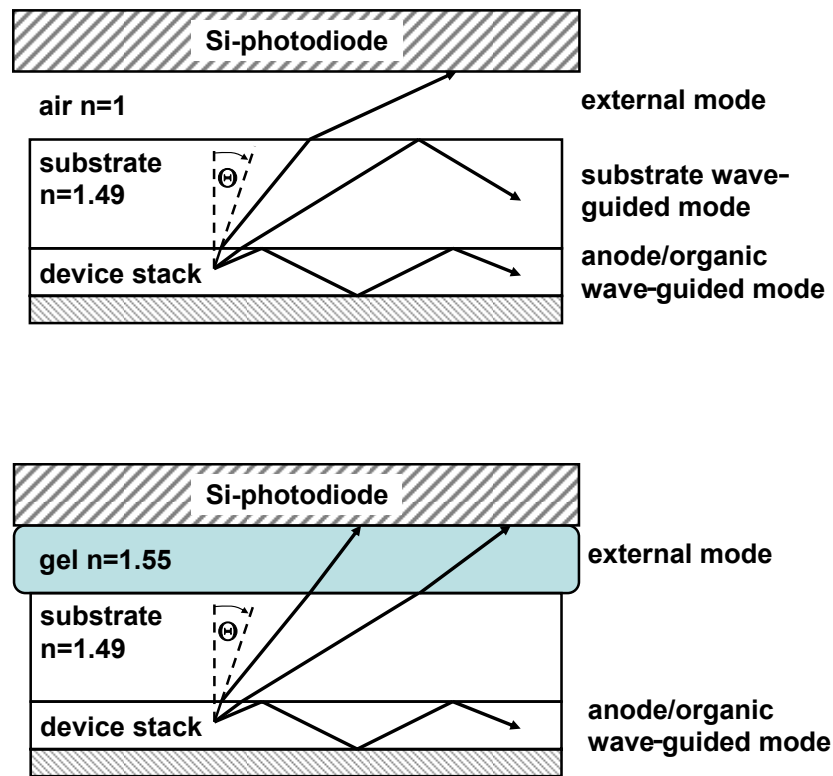


Fig. 4-3. Setup for measurement of external mode and substrate mode intensity: (a) Measurement of external mode intensity with the air gap. (b) When the gap is filled with gel, total internal reflection at the glass/air interface disappears, enabling the emitted light of the external and substrate wave-guided modes to be measured by the photodiode simultaneously.

4.2.B Results and Discussion

Fig. 4-4 shows the external light output of the devices as a function of the Alq_3 thickness before and after applying the BEF (measurement with air gap). It was independently confirmed that the emission from the device originated from $\text{Ir}(\text{ppy})_3$ with negligible (if any) emission from Alq_3 . It is observed that with increasing Alq_3 thickness the light output decreases in both cases (i.e., without and with the BEF). The intensity I_{air} , which is equal to the light output of the device before applying the BEF, decreases with increasing values of Alq_3 layer thickness to 1/3 of the output of the device without Alq_3 . Quasisinusoidal variation of current efficiency vs. Alq_3 thickness is attributed to the interference effect between direct emission and emission reflected from the metallic mirror of the electrodes (see chapter 2.2). This behaviour has already been reported [NakaT04], [Mats02]. However, the effect of light outcoupling *enhancement* due to the BEF is increased and shows a strong dependence on the

device structure itself. This enhancement is calculated and the results are shown in Table 4-1, where the values of a (given by $a = I_{\text{film}} : I_{\text{air}}$) are listed.

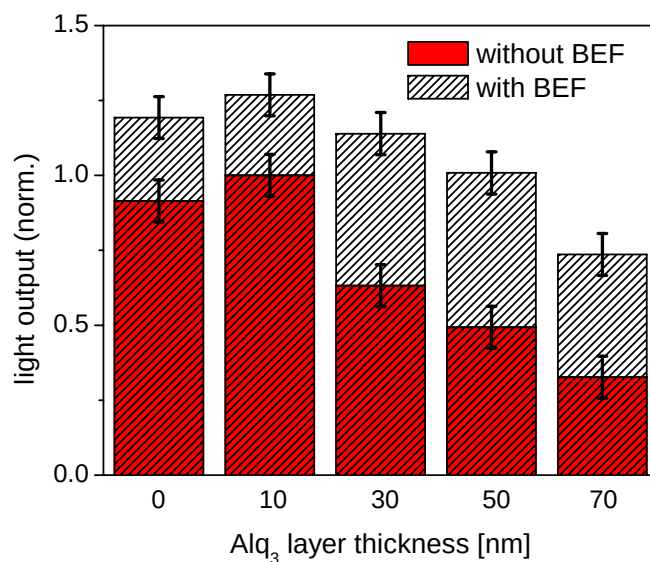


Fig. 4-4. Light output of the devices before and after applying the Brightness Enhancement Film. The intensities are normalized on the light output of the device with a Alq_3 layer thickness of 10 nm. The error bars represent the standard deviations of the measured values.

Table 4-1. Factor of apparent light outcoupling enhancement a .

Alq ₃ layer thickness	$a = I_{\text{film}} : I_{\text{air}}$
0 nm	1.30
10 nm	1.27
30 nm	1.80
50 nm	2.04
70 nm	2.25

A fraction of the wave-guided light retained within the substrate of the unmodified device (standard flat glass substrate) is extracted using a substrate surface modification. In order to investigate the dependence of a on the device structure, the intensity I_{gel} , which is equal to the sum of the external light output and the substrate wave-guided light, was measured for all (unmodified) devices as a function of the Alq_3 layer thickness. Fig. 4-5 shows the measured intensities I_{air} and I_{gel} . With increasing Alq_3 layer thickness, the intensity I_{gel} decreases to 2/3 of the value for the device without Alq_3 .

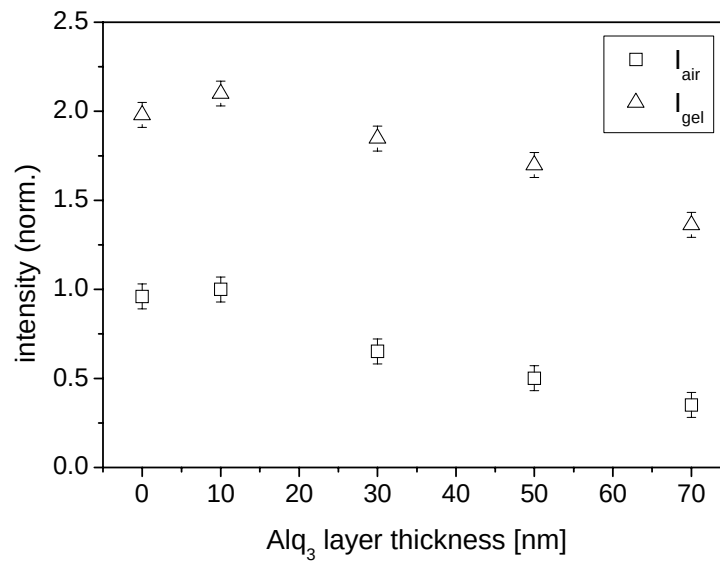
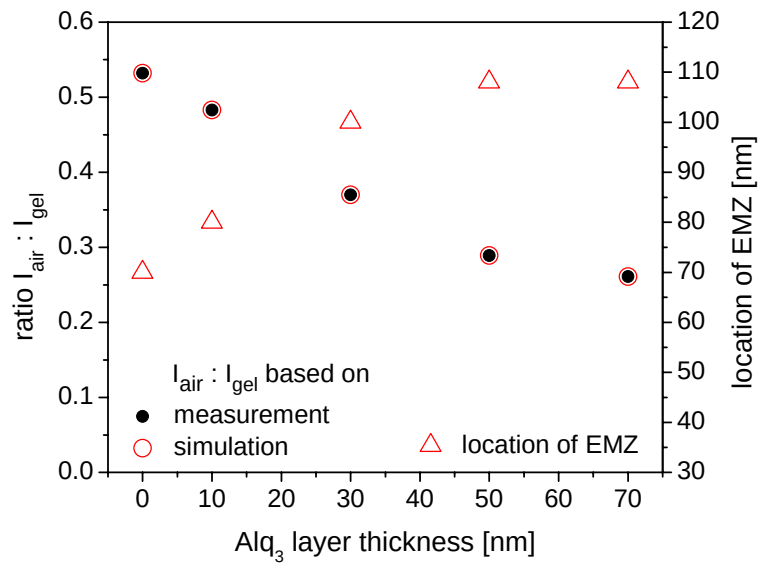


Fig. 4-5. The emission intensities detected by the Si photodiode at the air and gel gaps before substrate surface modification of the devices. The intensities are normalized on the output of the device with Alq_3 layer thickness of 10 nm. The error bars represent the standard deviation of the measured values.

Table 4-2 shows the ratio between the the substrate wave-guided light to the external light output for each device structure used in this study. This ratio is given by $I_{subst} : I_{air} = (I_{gel} - I_{air}) : I_{air}$. With increasing Alq_3 layer thickness, the fraction of substrate wave-guided light intensity increases compared to the fraction of the outcoupled light intensity. This was further studied by means of the optical simulation tool *UniMCO 4.0* described in chapter 2.2.

Table 4-2. Calculated amount of substrate wave-guided light I_{subst} and ratio $I_{subst} : I_{air}$

Alq ₃ -layer thickness	I_{air}	I_{gel}	$I_{subst} = I_{gel} - I_{air}$	ratio $I_{subst} : I_{air}$
0 nm	0.96	1.98	1.02	1.06
10 nm	1.00	2.10	1.10	1.10
30 nm	0.65	1.85	1.20	1.85
50 nm	0.50	1.70	1.20	2.4
70 nm	0.35	1.36	1.01	2.88

Fig. 4-6. Fit of the ratio I_{gel}/I_{air} based on the shown dependence of the location of the EMZ.

Using the simulation, the ratio $I_{air} : I_{gel}$ based on the measurements was fitted (Fig.4-6). This ratio was obtained by computing the flux into the external mode given by

$$(Eq. 4-1) \quad F_{ext} = \int_{z=z_1}^{z=z_1+d_{em}} \int_{\theta_{em}=0}^{\theta_{c1}=35^\circ} \int_{\lambda=0}^{\lambda=\infty} E(z) I_{em}(\theta_{em}, \lambda, z) 2\pi \sin \theta_{em} d\lambda d\theta_{em} dz,$$

and the flux into the substrate wave-guided mode given by

$$(Eq. 4-2) \quad F_{subs} = \int_{z=z_1}^{z=z_1+d_{em}} \int_{\theta_{c1}=35^\circ}^{\theta_{c2}=69^\circ} \int_{\lambda=0}^{\lambda=\infty} E(z) I_{em}(\theta_{em}, \lambda, z) 2\pi \sin \theta_{em} d\lambda d\theta_{em} dz,$$

where z_1 is the distance between the interface LEP-PBD layer and the cathode, and d_{em} is the thickness of the LEP (see chapter 2.2). I_{air} corresponds to F_{ext} and I_{gel} corresponds to the sum of F_{ext} and F_{subs} .

In order to compute the ratio based on simulation, the location of the emission zone (EMZ) in the device is needed. Here the location of the EMZ has been defined as the distance between the cathode and the center of a Gaussian distributed exciton profile within the light-emitting polymer with a full width at half maximum of 20 nm [Wu05] (see chapter 3.2 C). The distance between the EMZ and the cathode was varied to obtain the best fit. The resultant dependence of the location of the EMZ is shown in Fig. 4-6. The location of the EMZ obtained by the fit is also shown. Except for the prediction of the model for 70 nm thickness of Alq₃, it can be seen that the location of the EMZ scales with the actual device architecture.

The simulation as implemented above, used the ratio $I_{air}:I_{gel}$, which does not depend on the actual light outcoupled at the glass-air interface for each device. With the location of the EMZ obtained by the fit, one can now see the effect of device architecture on the extent to which light is outcoupled depending on the half-cavity defined by the OLED stack. Accordingly, Fig. 4-7 shows the measurements of the external light output and the computed light output of the unmodified devices as a function of Alq₃ layer thickness at a fixed current density. It is observed that the light output calculated here (red symbols) decreases steadily with increasing Alq₃ layer thickness. However, it is important to note that the experimentally measured light output (black symbols) shows a more exaggerated dependence on Alq₃ thickness. This is most likely due to variation in the internal device quantum efficiency as a function of Alq₃ thickness. In spite of this, the fit of $I_{air}:I_{gel}$ is more accurate. This is because the ratio $I_{air}:I_{gel}$ automatically eliminates the dependence on internal device efficiency.

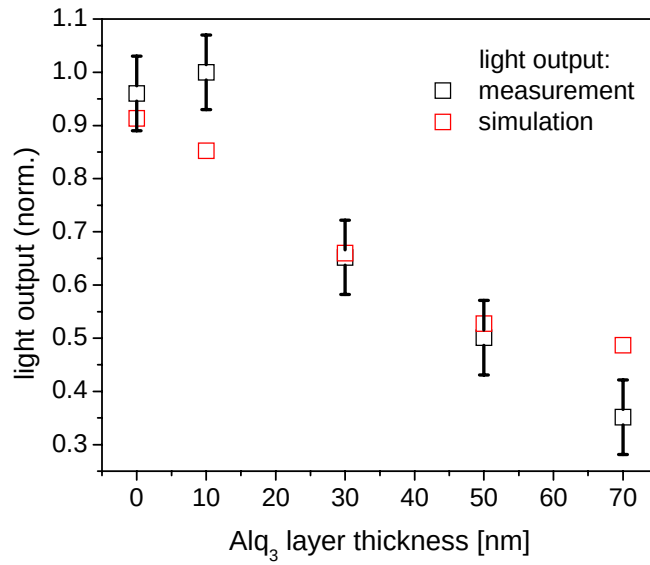


Fig. 4-7. Measurements of the external light output and computed light output as a function of Alq₃ layer thickness. The effect of different Alq₃ layer thickness on the intrinsic device efficiency is not considered for the simulated values.

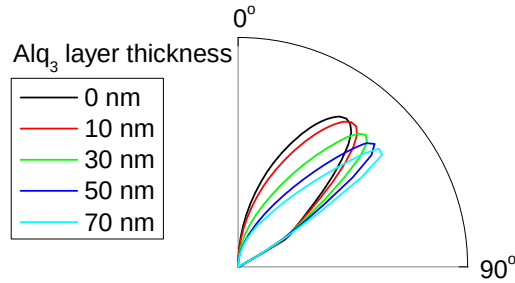


Fig. 4-8. Simulation of the internal flux as a function of emission angle θ_{em} integrated over all wavelengths for the devices used in this study. Each distribution is normalized on its maximum.

Fig. 4-8 shows the internal flux as a function of emission angle θ_{em} integrated over all wavelengths for the devices with different Alq₃ thicknesses, which was obtained by simulation using the values for the location of the EMZ determined by the fit. The internal flux as a function of emission angle $F_{in}(\theta_{em})$ is given by

$$(Eq. 4-3) \quad F_{in}(\theta_{em}) = \int_{z=z_1}^{z=z_1+d_{em}} \int_{\lambda=0}^{\lambda=\infty} E(z) I_{em}(\theta_{em}, \lambda, z) 2\pi \sin \theta_{em} d\lambda dz.$$

The angle of 0° corresponds to the direction normal to the substrate, where the angle of 90° corresponds to the direction parallel to the substrate. With increasing values of Alq_3 layer thickness, the distribution of intensity is shifted to higher angles with respect to the normal of the substrate (0°). As the intensity distribution shifts to higher angles, there will be an increase in light losses within the substrate due to total internal reflection.

The efficiency of light outcoupling by usual substrate surface modification techniques as a function of device architecture can be considered now. In the case of unmodified devices, with increasing Alq_3 layer thickness, the fraction of substrate wave-guided light compared to the fraction of the external light output increases (see Table 4-2) as a result of the shift of internal flux to higher angles (see Fig. 4-8). Only the photons, which are emitted by the LEP in a lower angle defined by the escape cone of the substrate, are extracted out of the device. After applying the BEF, photons of higher emission angles can be extracted due to the prismatic structure of the film. The higher the fraction of substrate wave-guided light the stronger is the light outcoupling enhancement of the BEF. Thus, the light outcoupling enhancement, obtained by calculating the ratio between the light output of the surface modified and the output of the unmodified device by itself, does not lead to accurate conclusions about the effectiveness of the light outcoupling method. Instead, the performance of the BEF can be determined by considering the ratio between the external output of the BEF coated device and the total amount of light, which is measured with the gel. This ratio is given by $I_{\text{film}} : I_{\text{gel}}$ and is approximately constant ($I_{\text{film}} : I_{\text{gel}} \approx 0.6$, see Table 4-3) for all device structures. By means of the BEF, about 60 % of the light, which is coupled into the substrate, is extracted out of each modified device. Via ray-tracing simulation it has been independently shown that this ratio is nearly independent from the angular distribution of emission when using a certain substrate surface modification for light extraction enhancement (see appendix C). The ratio $I_{\text{film}} : I_{\text{gel}}$ corresponds to the extraction efficiency η_{s-a} . This extraction efficiency η_{s-a} is defined as the fraction of photons coupled into the substrate, which is extracted into the ambient (i.e. the extraction efficiency from glass to air).

Table 4-3. Ratio between the output of the surface modified device and the light intensity, which is coupled into the substrate ($I_{\text{film}}/I_{\text{gel}}$).

Alq ₃ -layer thickness	$I_{\text{film}} : I_{\text{gel}}$
0 nm	0.63
10 nm	0.60
30 nm	0.63
50 nm	0.60
70 nm	0.58

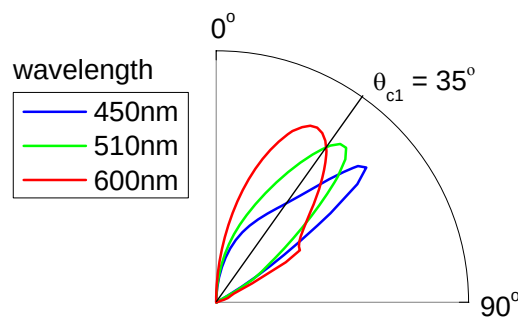


Fig. 4-9. Simulation of the internal flux as function of emission angle θ_{em} of the device without Alq₃ layer for the wavelengths 450 nm, 510 nm and 600 nm. Each distribution is normalized on its maximum.

In all the calculations above, the half-cavity effect was simulated over the entire range of wavelengths comprising the device spectrum. Furthermore, the dependence of the light outcoupling enhancement factor a (apparent light outcoupling enhancement) on the wavelength of the emitted light is discussed. The device without the Alq₃ layer is considered in this case. Fig. 4-9 shows the internal flux as a function of emission angle θ_{em} , which was calculated for light of wavelengths 450 nm, 510 nm and 600 nm using the micro cavity simulation. The internal flux as a function of emission angle θ_{em} for a certain wavelength is given by

$$(Eq. 4-4) \quad F_{in}(\theta_{em}, \lambda) = \int_{z=z_1}^{z=z_1+d_{em}} E(z) I_{em}(\theta_{em}, \lambda, z) 2\pi \sin \theta_{em} dz.$$

510 nm is the peak wavelength of the green emitter. The calculations for the wavelengths 450 nm and 600 nm were computed in order to obtain typical distributions for blue and red emission respectively. The internal flux for 450 nm is shifted to higher angles in comparison to the one obtained for 510 nm. Thus, it can be hypothesized, that the fraction of wave-guided light is higher for the blue emitting device than for the green emitting device. Hence, the light outcoupling enhancement due to substrate surface modification is higher for the blue emitting device than for the green emitting device. Contemplating the imaginary red emitting device, the internal flux of the red emitting device is shifted to lower angles. In this case, it can be hypothesized that the fraction of wave-guided light is lower than for the green emitting device. This leads to a lower light outcoupling enhancement for the red device due to the same substrate surface modification technique.

In particular, the dependence of light outcoupling enhancement on the wavelength has to be considered, when modifying the substrate surface of a device emitting in a broad range of wavelengths (for example, a white light-emitting device). In the case of a device with the structure and location of the EMZ discussed above, the light outcoupling enhancement is expected to be stronger in the shorter wavelength range of the spectrum. Thus, substrate surface modification can result in differences between the spectrum of the device before and after surface modification for light extraction.

4.3. Conclusion

It has been demonstrated that the apparent effectiveness of light outcoupling enhancement using a method of modifying the substrate surface, is significantly dependent on the device structure itself. This apparent effectiveness, however, is not the correct value to judge the effectiveness of a technique to enhance light outcoupling due to substrate surface modification. The ratio between the light output of the surface modified device and the total amount of light, which is generated in the device stack and coupled into the substrate (before the substrate/air interface), is a more accurate parameter to describe the light enhancement properties. In the optimal case the ratio is 1, which corresponds to a light outcoupling

methodology completely suppressing substrate wave-guiding. The determination of the enhancement properties using the proposed method not only allows the comparison of different methods of substrate surface modifying techniques, but also provides an analytical understanding to enable further improvement of each technique.

In contrast to the common misunderstanding that light outcoupling efficiency is about 22 % and independent from device architecture, the device data and optical modelling results clearly demonstrated that the light outcoupling efficiency is strongly dependent on the exact location of the recombination zone. Estimating the device internal quantum efficiencies based on external quantum efficiencies without considering the device architecture could lead to erroneous conclusions.

Further, a wavelength dependence of the apparent effectiveness of light outcoupling enhancement due to substrate surface modification has been shown. This is another reason why the apparent effectiveness is not the correct value to judge the effectiveness of a substrate surface modification. The dependence of the apparent light outcoupling enhancement leads to changes in the output spectrum, when modifying the substrate surface of an organic EL-device emitting in a broad range of wavelengths.

5. Down-Conversion OLEDs

In this chapter bottom emitting down-conversion OLEDs are studied from an optical point of view. The physical processes occurring in the down-conversion layer are translated into a ray-tracing model. The methods to obtain the relevant model inputs are described. The model is confirmed by comparing its predictions to experimental results. A blue emitting PLED panel optically coupled to a series of down-conversion layers is used for the experiments. Based on results obtained from ray-tracing simulation, some of the implications of the model for the performance of down-conversion OLEDs are discussed. In particular, it is analysed how the effective reflectance of the underlying blue OLED and the particle size distribution of the phosphor powder embedded in the matrix of the down-conversion layer influence extraction efficiency. Room for improvement and challenges in the design of down-conversion OLEDs are identified. Furthermore, an approach to improve angular color homogeneity of down-conversion devices is demonstrated. Finally, the realization of the down-conversion concept in OLED lighting technology is discussed. Thereby, challenges in the accomplishment of down-conversion OLEDs are discussed.

5.1. Optical Analysis of Down-Conversion OLEDs

Fig. 5-1 shows the basic physical processes which occur in the phosphor layer of a down-conversion device. These processes can be illustrated by following the optical pathways of different photons emerging from the active layers of the OLED into the substrate: A photon emitted by the blue OLED can be absorbed by the phosphor and re-emitted at a longer wavelength (photon A in Fig. 5-1). The re-emission of an absorbed photon holds off in the case of non-radiative decay of the excited state in the phosphor material (photon B). Photon C in Fig. 5-1 has reached the interface between phosphor layer and air with an angle of incidence exceeding the critical angle and undergoes total internal reflection. The photon then impinges a phosphor particle and is back-scattered toward the interface. This time, the angle of incidence is less than the critical angle and the photon is transmitted across the interface. Photon D is back-scattered into the active layers of the OLED device. After reflection at the

OLED's cathode, the photon is extracted into air. However, a photon which has been back-scattered into the active layers can be absorbed by the organic layers or by the electrodes (photon E).

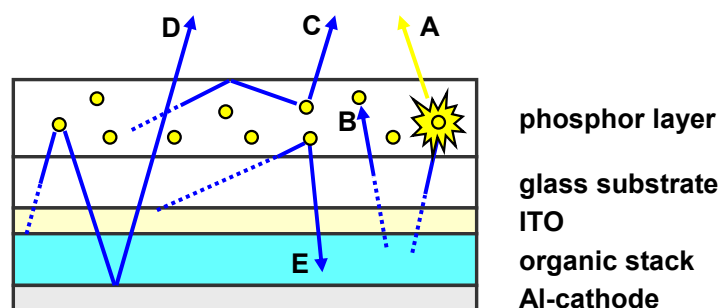


Fig. 5-1. Physical processes in the down-conversion layer: (A) absorption and re-emission by a phosphor particle, (B) absorption by a phosphor particle and non-radiative decay of the excited state in the phosphor material, (C) scattering by a phosphor particle leading to photon extraction into air, (D) reflection at the cathode, (E) absorption in the active layers of the OLED.

5.1.A Ray-Tracing Model of a Down-Conversion OLED

Description of the Ray-Tracing Software Light Tools

The physical processes in the down-conversion layer were translated into a ray-tracing simulation. Simulations were performed using the Monte-Carlo-based ray-tracing software *Light Tools* obtained from Optical Research Associates [ORA]. This software allows defining geometric objects in a three dimensional space. The optical properties of the bulk of these objects (i.e. refractive index and transmission) and of their surfaces (for example the reflectivity of a surface) can be set to simulate ray paths of light as they traverse through and within the objects according to classical ray optics. A light source related to a user-defined angular emission characteristic and emission spectrum can be placed within the objects. The wavelength and the propagation angle of a light ray emitted by the light source are determined by the Monte-Carlo-method (i.e. the emission spectrum and the angular emission characteristic are interpreted as probability distributions).

The software is capable to simulate scattering and absorption/re-emission processes at luminescence converting particles randomly distributed in the bulk of a geometric object. Here a mean free pathway *MFPW* defines the average distance between two impingements at

phosphor particles. The software varies the distance between two impingements randomly, while the average distance is kept equal to the set mean free pathway $MFPW$. The flow chart of the phosphor model of *Light Tools* is shown in Fig. 5-2. When a ray reaches a phosphor particle, the probability for its absorption is given by $P_{abs}(\lambda)$. The set quantum yield QY determines the re-emission of the absorbed light. The normalized re-emission spectrum of the phosphor as a function of wavelength is given by $S_c(\lambda)$. The angular distribution of the re-emitted light is isotropic. In the case of light scattering at a particle, the scattering angle is defined as the angular difference between the original and the new propagation direction of a light ray (Fig. 5-3). For each single scattering event, the set scattering function $p(\vartheta, \lambda)$ determines the new propagation direction of the light ray. The quantum yield of the phosphor and the ratio between absorption and scattering are interpreted by probabilities. Accordingly, the angular distribution of photon emission $D(\alpha)$, the normalized spectral distribution of the blue OLED $S_{OLED}(\lambda)$, the isotropic re-emission of the phosphor particles, the scattering function $p(\vartheta, \lambda)$ and the normalized re-emission spectrum of the phosphor $S_c(\lambda)$ are interpreted by probability distributions. This allows simulating the corresponding physical processes by means of the Monte-Carlo-method.

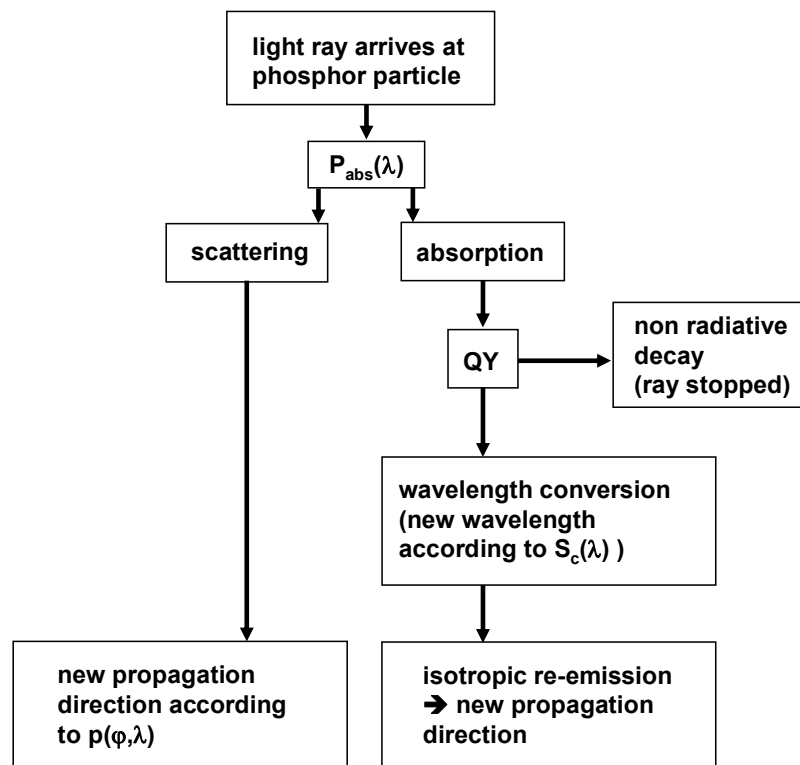


Fig. 5-2. Phosphor model in the optical simulation software *Light Tools*.

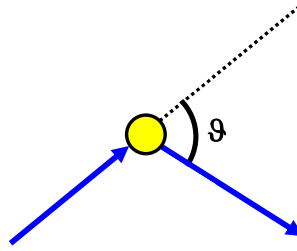


Fig. 5-3. The scattering angle is the angular difference between the original and the new propagation direction of a light ray after it has been scattered by a phosphor particle.

The rays simulated by *Light Tools* can be analysed by using so-called receivers, which count the number of rays hitting at a certain user-defined surface. A far field receiver surrounds the objects traversed by the rays in infinite distance. Therefore, this receiver counts all the rays leaving the considered geometrical structure into the ambient. Furthermore, the far field receiver is capable to count rays in certain ranges of solid angle and the corresponding spectral distribution of the rays within this ranges. This allows analysing the emission color of the simulated system as a function of viewing angle.

Representation of the OLED in the Ray-Tracing Simulation

In translating the physical structure of a down-conversion OLED to the ray-tracing simulation the down-conversion layer is represented by a cuboid. This cuboid has the refractive index n_{matrix} . Scattering, absorption and re-emission by the particles in the down-conversion layer are simulated according to the phosphor model of *Light Tools*. Here the mean free path way $MFPW$ between two impingements at particles is given by:

$$(Eq. 5-1) \quad MFPW = \frac{1}{N} \cdot \frac{1}{\bar{q}_{geo}},$$

where N is the phosphor particle density in the down-conversion layer and $\bar{q}_{geo}$ is the average geometric particle cross section.

In a real device, light generated by the OLED enters the down conversion layer at position $z = 0$ (see Fig. 5-4). In the model, an area light source with angular distribution of photon emission $D(\alpha)$ ($0^\circ < \alpha < 90^\circ$) is placed at the bottom side of the cuboid representing the down-conversion layer. This distribution corresponds to the angular distribution of

emission in the substrate of a real OLED. The normalized spectral distribution (in photons⁶) of this light source is given by $S_{OLED}(\lambda)$. The OLED layers are represented by one single layer forming the bottom of the cuboid. This layer has the reflectance $R_{OLED}(\lambda)$, which is the effective reflectance of the active layers as a function of wavelength. In the model, this reflectance $R_{OLED}(\lambda)$ is set to be independent from the angle of incidence.

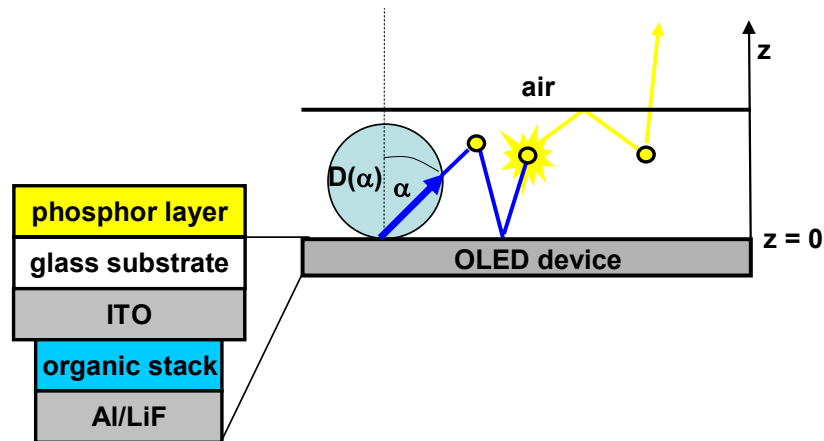


Fig. 5-4. Schematic illustration of the ray-tracing model of a down-conversion OLED. In the model, the OLED layers are grouped into a single layer.

On the top side of the cuboid, the critical angle for total internal reflection at the interface between down-conversion layer and air acts as the criterion of photon extraction into the ambient. According to Snell's law, the critical angle is given by

$$(Eq. 5-2) \quad \alpha_{crit}(\lambda) = \sin^{-1}\left(\frac{1}{n_{matrix}(\lambda)}\right).$$

The flowchart in Fig. 5-5 outlines the simulation of the propagation of a photon in the down-conversion layer in order to summarize the model as described above.

⁶ The spectral *photon* distribution of OLED emission and the spectral *photon* distribution of phosphor re-emission are needed as input for the simulation. The optical pathways of photons are computed in the ray-tracing simulation. The use of the spectral *power* distribution as input would lead to erroneous results due to the fact that the Stokes shift of wavelength conversion is not regarded in the phosphor model of Light Tools.

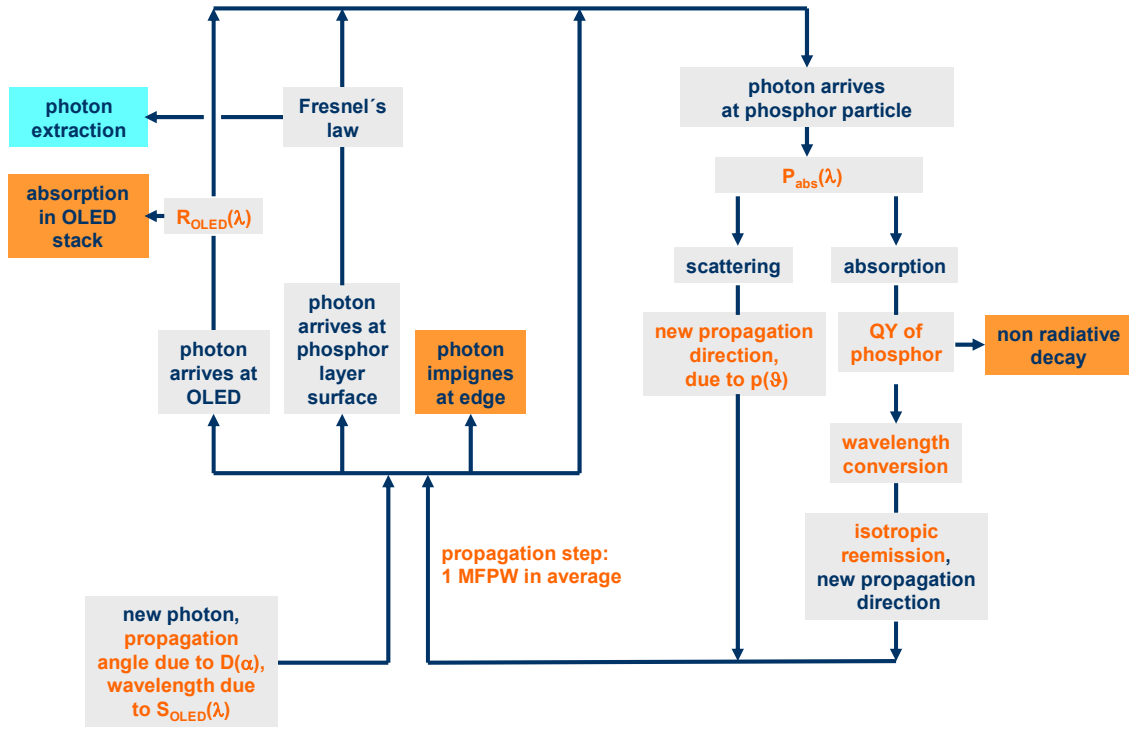


Fig. 5-5. Flow chart of the simulation based on the proposed model. All processes simulated by the Monte-Carlo-method are printed in red letters.

In this ray-tracing model of a down-conversion OLED, various simplifying approximations were made in effort to minimize and simplify the number of model input parameters. In particular, these approximations are:

- The OLED active layers are grouped into a single layer with the effective reflectance $R_{OLED}(\lambda)$. Hence in the model, the “light source” is a photon emitting area, which is located at the position $z = 0$ (see Fig. 5-4). The light source sends out photons into the down-conversion layer in an angular photon distribution $D(\alpha)$.
- The effective reflectance of the OLED active layers $R_{OLED}(\lambda)$ is set to be independent from angle.
- The normalized spectral distribution of the light emitted by the blue OLED, $S_{OLED}(\lambda)$, is assumed to be independent from angle.
- All interfaces are considered to be planar in the model.
- Substrate edge emission is neglected, i.e. all photons reaching the lateral border of the device are counted as absorbed.
- Absorption in the matrix material embedding the phosphor is neglected, i.e. the matrix material is regarded as completely transparent.

In the simulation, light in the range of wavelengths from 380 nm to 780 nm is considered in steps of 5 nm. The simulation software *Light Tools* allows computing the output spectra as a function of viewing angle by means of a far field receiver. The spectral distributions of photons leaving the conversion layer in certain ranges of solid angle with respect to the substrate normal are determined. In particular, these ranges are from 0° to 15°, from 15 to 25°, from 25° to 35°, from 35° to 45°, from 45° to 55°, from 55° to 65°, and from 65° to 75°.

Furthermore, the far field receiver counts the number of rays leaving the down-conversion layer. The ratio between this number and the total number of rays emitted by the light source corresponds to the fraction of photons coupled into the substrate which is extracted into the ambient. Hence, in this consideration the total extraction efficiency of the device η_{ph} (see chapter 2.1.B) is decomposed into two components, i.e.:

$$(Eq. 5-3) \quad \eta_{ph} = \eta_{OLED-s} \eta_{s-a},$$

where η_{OLED-s} is the fraction of the generated photons that is coupled into the substrate, and η_{s-a} is the fraction of photons coupled into the substrate which is extracted into the ambient. This decomposition is analogous to the distinction made between ITO/organic and substrate wave-guided modes (see chapter 2.2 A) and also analogous to the general method to evaluate substrate surface modification techniques proposed in chapter 4. Here the latter term is the primary focus. The effects of volumetric light scattering and phosphor absorption/re-emission upon the fraction of light emitted into the ambient η_{s-a} are considered in particular.

5.1.B Determination of Model Inputs, Sample Fabrication

In order to confirm the model, its predictions were compared to experimental results. Therefore a deep blue emitting polymer OLED panel and two sets of down-conversion layers applied on free-standing glass substrates were fabricated. The sample fabrication and the measurements of the relevant physical properties of the OLED device are described in this section. Furthermore, the methodology aimed at obtaining the optical characterization of the phosphor is outlined.

Fabrication of the Blue OLED Panel

The blue emitting OLED panel had an active area of 4.2 cm x 3.3 cm⁷. Additionally a smaller OLED (active area: 0.5 cm x 0.5 cm) with the same architecture (i.e. same layer thicknesses) was fabricated, which was necessary for the determination of the angular distribution of photon emission, $D(\alpha)$ (see below, paragraph “Emission Characteristics of the Blue OLED”). The OLED structure consisted of a glass substrate, 120 nm indium tin oxide (ITO), 120 nm poly(3,4)-ethylenedioxythiophene doped with poly(styrene sulfonate) (PEDOT:PSS), 80 nm deep blue light-emitting polymer and a Ba/Al cathode. The PEDOT:PSS was supplied by H.C. Starck. The organic layers were applied by spin-coating on ITO coated float glass substrate (refractive index $n_g = 1.52$). The cathode was applied by thermal evaporation through a shadow mask in a vacuum chamber under standard conditions. Deposition of the OLED stack was followed by encapsulation with a glass lid.

Fabrication of Down-Conversion Layers

A silicone was used as matrix material of the down-conversion layer. The refractive index of the silicone n_{matrix} (see appendix F, Fig. F-4) was close to the refractive index of the OLED substrate ($n_g = 1.52$) and it had a transmission of 98 % through a sample of 1 mm thickness within the range of the visible spectrum. YAG:Ce³⁺ phosphor (quantum yield of luminescence conversion $QY > 0.95$, [Berb06]) obtained from OSRAM GmbH was used as luminescence converting material. By means of both a two axis rotary high-speed mixer and a masticator, the phosphor particles were thoroughly dispersed in the silicone matrix. This mixture was then applied on a glass substrate by means of the doctor blade technique using an Elcometer 4340 Film-Applicator. The thickness of the film was controlled by adjusting the gap between the doctor blade and the substrate. The film was cured 60 min at 150 °C. Two

⁷ The dimensions of the OLED panel used in the experiments were set for the device geometry in the ray-tracing simulation.

sets of films were fabricated this way. The first set (samples A1-5) had a phosphor concentration of 15.3 percent by volume, the second set (samples B1-4) a concentration of 20.3 percent by volume. The final thickness of the down-conversion layer was determined by a tactile thickness measuring gage (KLA-Tencor P12) at three spots of each film. The layer thicknesses of the first set of films were 17, 23, 49, 71 and 102 μm , the thicknesses of the second set were 18, 23, 55 and 70 μm . Table 5-1 summarizes the results of the thickness measurements.

Table 5-1. Thickness measurements of the down-conversion layers.

sample	measurement 1 [μm]	measurement 2 [μm]	measurement 3 [μm]	average film thickness [μm]	standard deviation [μm]
A1	17.9	15.9	16.5	16.8	0.99
A2	22.3	23.2	22.9	22.8	0.48
A3	49.4	48.7	47.5	48.5	0.95
A4	70.1	72.0	71.1	71.1	0.94
A5	100.4	102.2	102.8	101.8	1.25
B1	17.7	18.4	17.3	17.8	0.58
B2	23.0	22.1	23.1	22.7	0.54
B3	53.7	54.5	55.9	54.7	1.12
B4	70.7	70.2	69.1	70.0	0.79

Emission Characteristics of the Blue OLED

The angular dependence of the OLED light output as it goes from the OLED layers into the substrate, cannot be measured directly due to refraction and total internal reflection at the interface between glass substrate and air. To determine $D(\alpha)$, the small OLED (active area 0.5 cm x 0.5cm) was coupled to the center of a glass hemisphere (diameter 25 mm) by using a refractive index matching gel (Norland Optical Adhesive NOA 68). The emitted light was probed as a function of angle (steps of 5°) from the hemisphere by a spectral camera Photo Research PR650. This geometry effectively makes the emission angle in glass equal to the emission angle in air. Hence, basically all photons hit the surface of the glass hemisphere at an angle of 90°. This allows the measurement of the OLED emission within the substrate at angles exceeding the critical angle of totally internal reflection between glass and air (Fig. 5-6) [Lu02], [Bulo98]. As the result of the measurement, Fig. 5-7 shows the angular light output emitted by the blue OLED into the glass substrate. The spectra measured as a function of angle from the hemisphere, showed a blue shift from CIE x/y = 0.164/0.124 at 0° to CIE x/y = 0.162/0.042 at 70°; emission color and intensity as a function of angle are determined by the half-cavity formed by the OLED stack (see chapter 2.2). The integrated spectral distribution of emission within the substrate is depicted in the inset of Fig. 5-7. To obtain this integrated spectrum, the spectra as a function of angle were weighted with their contribution to the total light output and summed up. As input for the simulations presented in chapter 5.1.C, the distributions $D(\alpha)$ and $S_{OLED}(\lambda)$ (in photons) were derived from the data plotted in the graphs of Fig. 5-7.

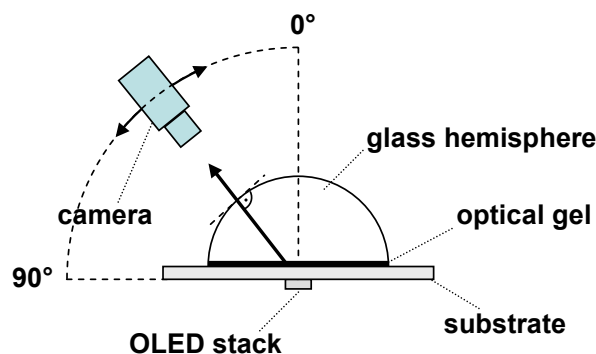


Fig. 5-6. Setup for the measurement of the angular distribution of OLED emission within the substrate.

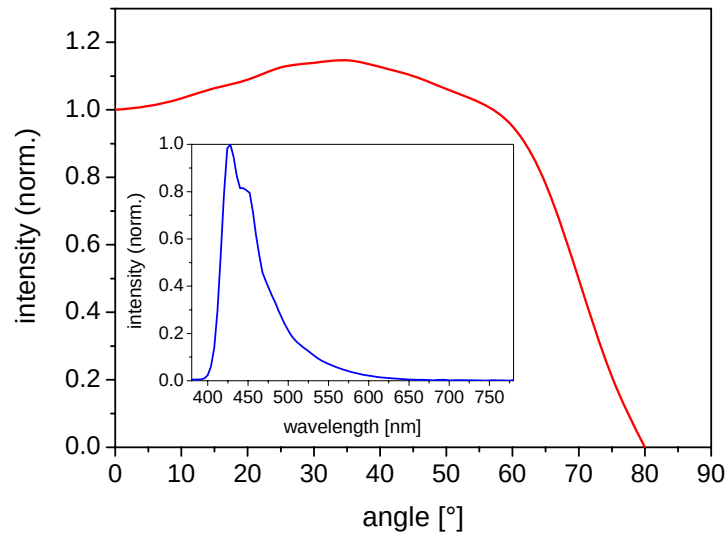


Fig. 5-7. Angular distribution of emission within glass substrate of the blue OLED. The inset shows the integrated spectral distribution of OLED emission within the substrate.

Effective Reflectance of the OLED Panel

The effective reflectance of the OLED panel $R_{OLED}(\lambda)$ was measured using a Perkin-Elmer reflectometer Lambda 950 at angles of 8°, 30° and 60° with respect to the substrate normal. The reflectance as a function of wavelength at the different angles is plotted in the graph in Fig. 5-8. In general, the resulting reflectance of a thin film structure depends on the angle of incidence due to interference effects. However, the measurements of the reflectance $R_{OLED}(\lambda)$ at 8°, 30° and 60° show a similar slope and differ only by 10 % at most. The low reflectance in the 400 nm wavelength region is given by the absorbance of the blue emitting polymer. At higher wavelengths, the effective reflectance of the OLED is mainly determined by the transmittance of the ITO anode and the reflectance of the aluminum cathode. Considering the minor variations in the measured angular reflectance, the effective reflectance is set to be independent from the angle of incidence in the simulation. The reflectivity at the angle of 30° is used as input for the simulations presented in chapter 5.1.C.

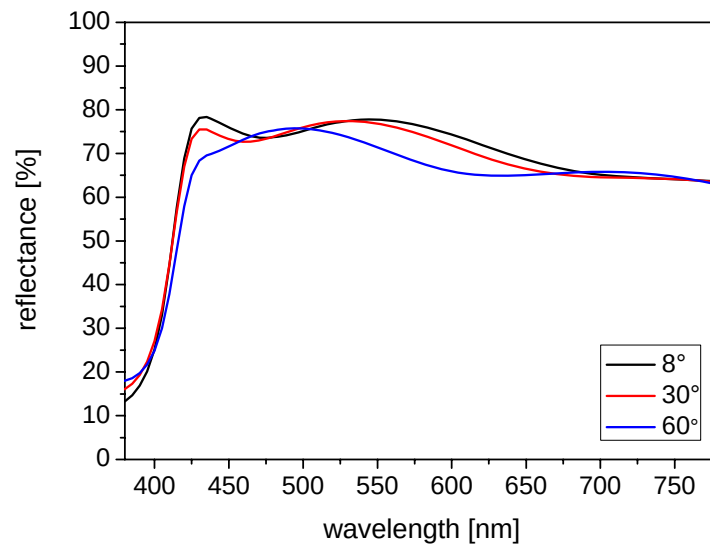


Fig. 5-8. The reflectance of the OLED-panel $R_{OLED}(\lambda)$ measured at angles of 8° , 30° and 60° with respect to the substrate normal.

Characterization of the Phosphor Powder

In the ray-tracing model the behaviour of a photon impinging a phosphor particle is determined by the average single scattering/absorption characteristics in the matrix material (see chapter 2.5.B). In particular, the average single scattering characteristics are the average scattering function, the average scattering cross section and the average absorption cross section. As described in chapter 2.5, one needs knowledge about the refractive index of the embedding matrix, the complex refractive index of the phosphor and its particle size distribution for the computation of these characteristics. The particle morphology, on the other hand, is hardly of importance, since the statistic orientation of large amounts of non-spherical powder particles allows a description in terms of an “effective” particle size of spherical particles [Pipr07].

The optical characterization of the YAG:Ce^{3+} powder used for the down-conversion layers was performed by OSRAM GmbH as follows [Berb06]: The phosphor particle size distribution was determined by a method utilizing sedimentation in a viscous gradient. The gradient was built inside a centrifuge. This way the determination of the particle size is conducted by measuring the time required to sink a defined distance. The relative amount of particles at the respective particle size is given by the amount of extinction detected by a

photo sensor. For this method knowledge about the density of the phosphor material is needed, or a reference sample of particles of same density has to be used for calibration.

The determination of the complex index of refraction of the phosphor powder $n_{phos}^*(\lambda)$ is challenging due to the fact, that most phosphors are only available as powders. For conventional methods sample sizes in the magnitude of several millimeters are needed. Thus these methods are only suitable for bulk materials. Standard techniques to determine the refractive index of a powder sample are based on the immersion of small particles in a set of liquids with exactly defined refractive indices. The refractive indices of typical phosphor materials are in the range of $n = 2$. Liquids in this range contain large amounts of arsenic leading to challenges in their handling. Furthermore, only the real part of the refractive index is determined by means of immersion techniques.

The determination of the complex refractive index of the YAG:Ce³⁺ powder used for the down-conversion layers was performed by an alternative approach to the direct experimental determination of the optical properties. The determination according to this method is conducted as follows [Pipr07]: First the re-emission spectrum of a powder plaque with a defined volume fill factor (in the range between 40 % and 50 %) was measured. The setup of the measurement was translated into a computer model. Literature values for the refractive index of the host lattice of the phosphor material (i.e. YAG for YAG:Ce³⁺) and the particle size distribution determined as described above were used as input parameters for the simulation. A first curve progression for the imaginary component of $n_{phos}^*(\lambda)$ can be derived by applying the Kubelka-Munk function (see appendix A) on the measurement of the powder reflectance. The simulation software computes the average scattering characteristics of the phosphor powder according to MIE-theory and simulates the behaviour of the powder plaque, i.e. the simulation gives a first re-emission spectrum. The first simulation result will most likely differ from the measured re-emission spectrum. By introducing physically reasonable absorption bands of various kinds, the complex refractive index is altered until the simulation fits the measurements sufficiently.

Based on the measurements of the particle size distribution, based on the complex refractive index of the phosphor (determined as described above) and based on the refractive index of the silicone used as matrix of the down-conversion layers (see appendix E), the average single scattering characteristics in silicone as surrounding medium were computed according to MIE-theory in the spectral range from 380 nm to 780 nm in steps of 5 nm. As a result of this computation, Fig. 5-9 shows the plot of the average scattering function $\bar{p}(\vartheta)$ for

wavelengths 420 nm, 530 nm, 600 nm, and Fig. 5-10 shows the plot of the average absorption probability as a function of wavelength, $P_{abs}(\lambda)$, which is given by:

$$(Eq. 5-4) \quad P_{abs}(\lambda) = \frac{\overline{Q}_A(\lambda)}{\overline{Q}_A(\lambda) + \overline{Q}_S(\lambda)},$$

where $\overline{Q}_A(\lambda)$ is the average absorption cross section of the particle as a function of wavelength, and $\overline{Q}_S(\lambda)$ is the average scattering cross section as a function of wavelength.

Additionally, the phosphor luminescence spectrum is depicted in the inset of Fig. 5-10.

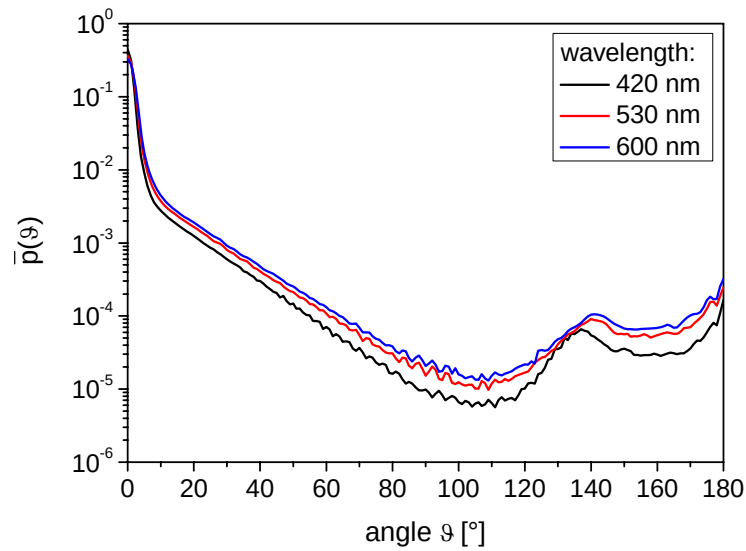


Fig. 5-9. Plot of the average scattering function $\overline{p}(\theta)$ of the phosphor powder in silicone as the surrounding medium calculated for wavelengths 420 nm, 530 nm and 600 nm.

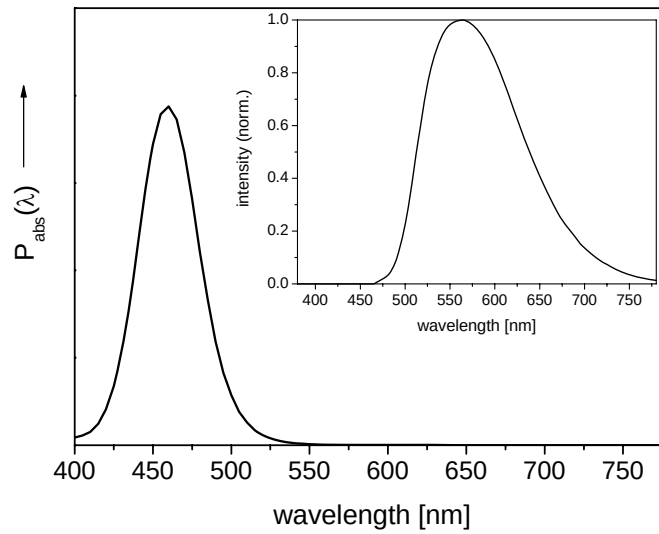


Fig. 5-10. Plot of the average absorption probability as a function of wavelength for silicone as the surrounding medium. The inset shows the luminescence spectrum of YAG:Ce³⁺ (excitation wavelength 460 nm). The data was obtained from OSRAM GmbH [Berb06].

5.1.C Experimental Confirmation of Model, Interpretation

Average Single Scattering Characteristics

In the ray-tracing simulation presented in this work, scattering and absorption by particles are simulated according to the average single scattering/absorption characteristics which have been obtained by the fit on the re-emission measurement of the powder plaque. It was independently confirmed that the computed average scattering function is an appropriate description of the change in the propagation angle of photons which are scattered at the phosphor particles within the silicone matrix, i.e. the correctness of this set of parameters was tested by simulating a well-defined geometrical setup. The angular dependence of light scattering of a collimated light beam incident on freestanding conversion layers was measured. The measurements were compared to model predictions obtained by ray-tracing simulation based on the average single scattering/absorption characteristics.

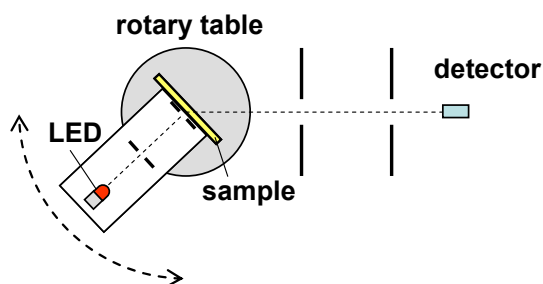


Fig. 5-11. Setup for the measurement of the angular dependence of light scattering of a collimated light beam incident on a conversion layer.

Fig. 5-11 shows the setup of the measurements. A red emitting high power LED (*Golden Dragon* obtained from OSRAM Opto Semiconductors, dominant wavelength 625 nm, light output: 10 lm at 100 mA) was used as light source⁸. A lens optically coupled to the LED provided enhanced front emission. Two apertures placed between the LED and the freestanding conversion-layer ensured the normal incidence of a collimated light beam on the sample⁹. This configuration was fixed on a rotary table whose axis of rotation ran through the conversion layer. The angular dependence of light scattering was probed by a glass fibre coupled to a spectrometer (Instrument Systems CAS 140 B). The angular resolution of the system was at least $\sim 2^\circ$. The measurements were repeated at 3 different positions on each sample.

The comparative ray-tracing simulations were performed using a modification of the model described in section 5.1.A. Here the reflecting layer representing the OLED layers and the light source with the angular distribution of emission $D(\alpha)$ were removed from the model. Instead light rays (wavelength 625 nm) were sent into the conversion layer in the direction of the sample normal. On the other side of the sample, the scattered rays were collected by a infinite far field detector, which counted the rays in an angular resolution of 1° at an infinite distance to the sample.

⁸ A red emitting LED has been chosen for the experiment, because there is no absorption by the phosphor in this range of wavelength, which simplifies the analysis of the measurements.

⁹ As a result of the geometry of the apertures and their placement, the maximum deviation of the light beam from the normal of the sample was 0.5° .

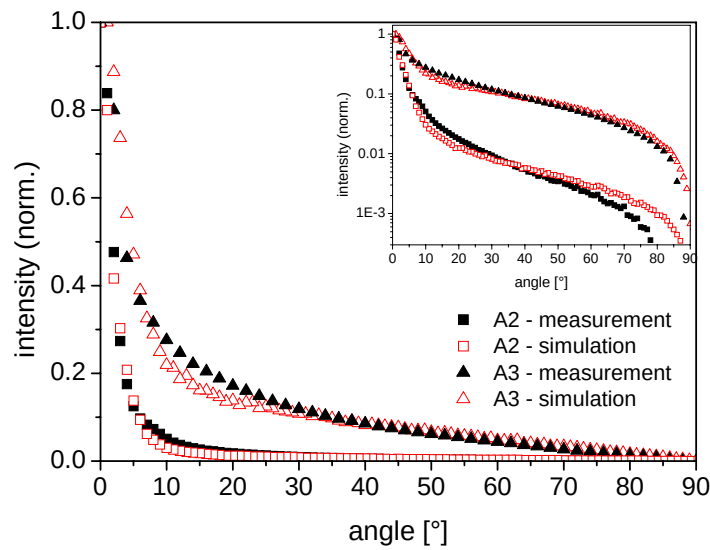


Fig. 5-12. Measurement and ray-tracing simulation of angular dependence of light scattering of a collimated light beam incident on the conversion layers A2 and A3. The inset shows the same data in a logarithmic plot.

Fig. 5-12 shows the measurements of the angularly resolved intensity versus angle for conversion layers A2 and A3. In addition the results of the comparative ray-tracing simulations are plotted. Clearly, the plots obtained from simulation provide an acceptable reproduction of the measurements, which confirms the average scattering function as an appropriate description of scattering within the layer. Furthermore it can be seen, that the slope of the intensity versus angle is dependent on the layer thickness. In comparison to layer A2, layer A3 leads to a more pronounced deflection from the cumulated light beam¹⁰. This is due to the longer optical path through layer A3, which leads to a higher probability of a light ray being scattered by the phosphor.

¹⁰ The presented measurements and simulation evoke a critical view on the reference [Bath07], where a method for the determination of the scattering function of scattering particles in a diffuse layer is proposed. Here the angular dependence of light scattering of a collimated light beam incident on freestanding diffusive layers was measured by using a similar setup as described above. The scattering function was determined via a non-linear fit of the Henyey-Greenstein scattering function [see appendix D] on the measurements. However, the influence of the layer thickness was neglected when performing the fit and, consequently, it is questionable, if the derived scattering function is a suitable description of scattering at a single particle within the layer.

Output Spectrum of Down-Conversion Device

The glass substrates carrying the down-conversion layers were optically coupled to the blue emitting OLED panel by using an optical gel (Norland Optical Adhesive 68, refractive index $n = 1.54$). The emission of the panel with and without down-conversion layers was measured as function of the angle with respect to the substrate normal. The emission was probed by a Photo Research PR650 spectral camera in steps of 10° . All measurements were carried out at a fixed current of 20 mA. While performing the measurements, it was confirmed that there was no decrease in the light output of the OLED-panel caused by degradation processes in the active layers.

Fig. 5-13 shows the integrated spectrum of the down-conversion device comprising the blue panel and layer A3 as derived from measurements. To obtain this integrated spectrum, the spectra measured as a function of viewing angle were weighted with their contribution to the total light output and summed up. Furthermore, the corresponding integrated spectrum obtained from simulation is depicted in Fig. 5-13. In the simulation, the extracted photons were collected by means of the far field receiver. There is good agreement in the slopes of both spectral distributions. However, the height of the simulated blue peak deviates by 6 % from the peak height of the spectrum obtained from measurements. This can be explained by both the spectral resolution of the simulation (5 nm) limited by PC hardware performance and the spectral resolution of the PR650 camera (4 nm) leading to non exact representation of narrow peaks.

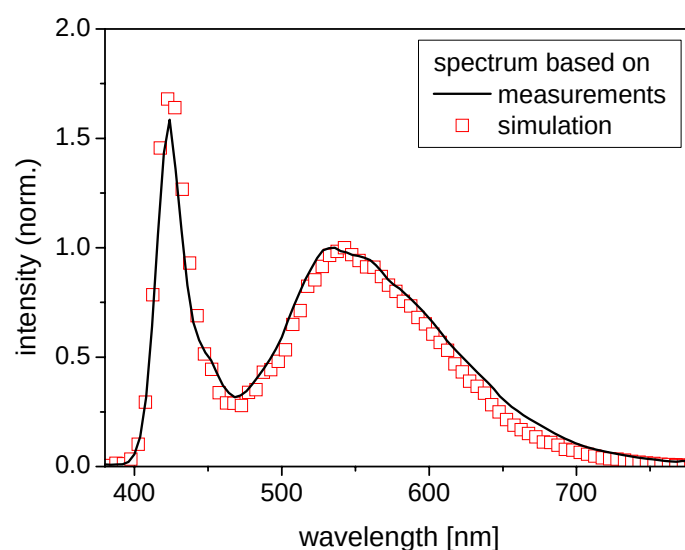


Fig. 5-13. Integrated spectrum based on measurement in comparison to the simulation result for the blue panel equipped with the conversion layer A3.

Additionally, Fig. 5-14 gives an overview of the CIE-coordinates related to the integrated spectra, which were obtained from simulation and measurements of all conversion layers used in this study. The graph proves the good agreement between simulation and experimental results in a broad range of conversion layer thickness.

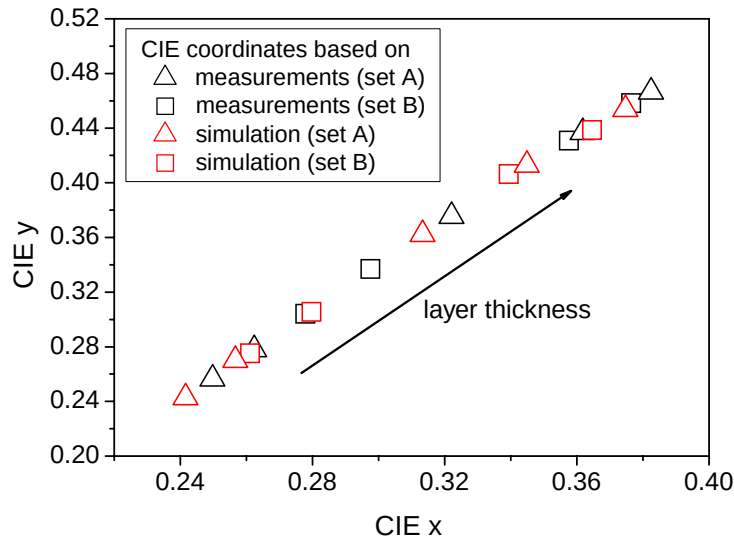


Fig. 5-14. Plot of the CIE-coordinates related to the integrated spectra, which were obtained from simulations and measurements for all conversion layers used in this study.

It is considered additionally, how sensitive the human sensation of emission color is to variations in conversion layer thickness. Contemplating a certain target color of device emission (given by $\text{CIE } x/y = x_{\text{target}}/y_{\text{target}}$), the variation $\pm \Delta x$ and the variation $\pm \Delta y$ are defined as the highest allowable deviations from the target emission color in terms of the CIE x/y coordinates. No change of emission color should be detectable by the human eye in this range. In this consideration, Δx and Δy are derived by the Mc Adam ellipse¹¹ located at the target color coordinates: $2 \Delta x$ corresponds to the projection of this ellipse onto the x -axis of the 1931 CIE chromaticity diagram, and $2 \Delta y$ corresponds to the projection onto the y -axis. In the graphs of Fig. 5-15, the CIE x -coordinate and the CIE y -coordinate of emission color are plotted as a function of conversion layer thickness as obtained from measurements and simulations for layer set A. In the magnified plots in Fig. 5-15 b/d, a whitish target color in

¹¹ The Mc Adam ellipse related to a certain color gives the range in the 1931 CIE chromaticity diagram, in which the human eye is not capable to distinguish differences from this color. Size and orientation of the Mc Adam ellipse depends on the location in the chromaticity diagram [Rich76].

the range of CIE $x_{target}/y_{target} = 0.32/0.37$ is contemplated. Here Δx is ≈ 0.0015 and Δy is ≈ 0.003 , according to the definition given above. Comparing the plot in Fig. 5-15b to the plot in Fig. 5-15d, the maximum allowable range of conversion layer thickness Δt is determined by the CIE x-coordinate of emission as a function of layer thickness ($\Delta t_x < \Delta t_y$). In the range of target color coordinates $x_{target}/y_{target} = 0.32/0.37$, the maximum allowable range of conversion layer thickness, derived from experimental data, is $\Delta t_{mx} = 48.3 \mu\text{m} - 46.9 \mu\text{m} = 1.4 \mu\text{m}$. The simulation-based result $\Delta t_{sx} = 53.4 \mu\text{m} - 51.5 \mu\text{m} = 1.9 \mu\text{m}$ is in the same magnitude of order as Δt_{mx} .

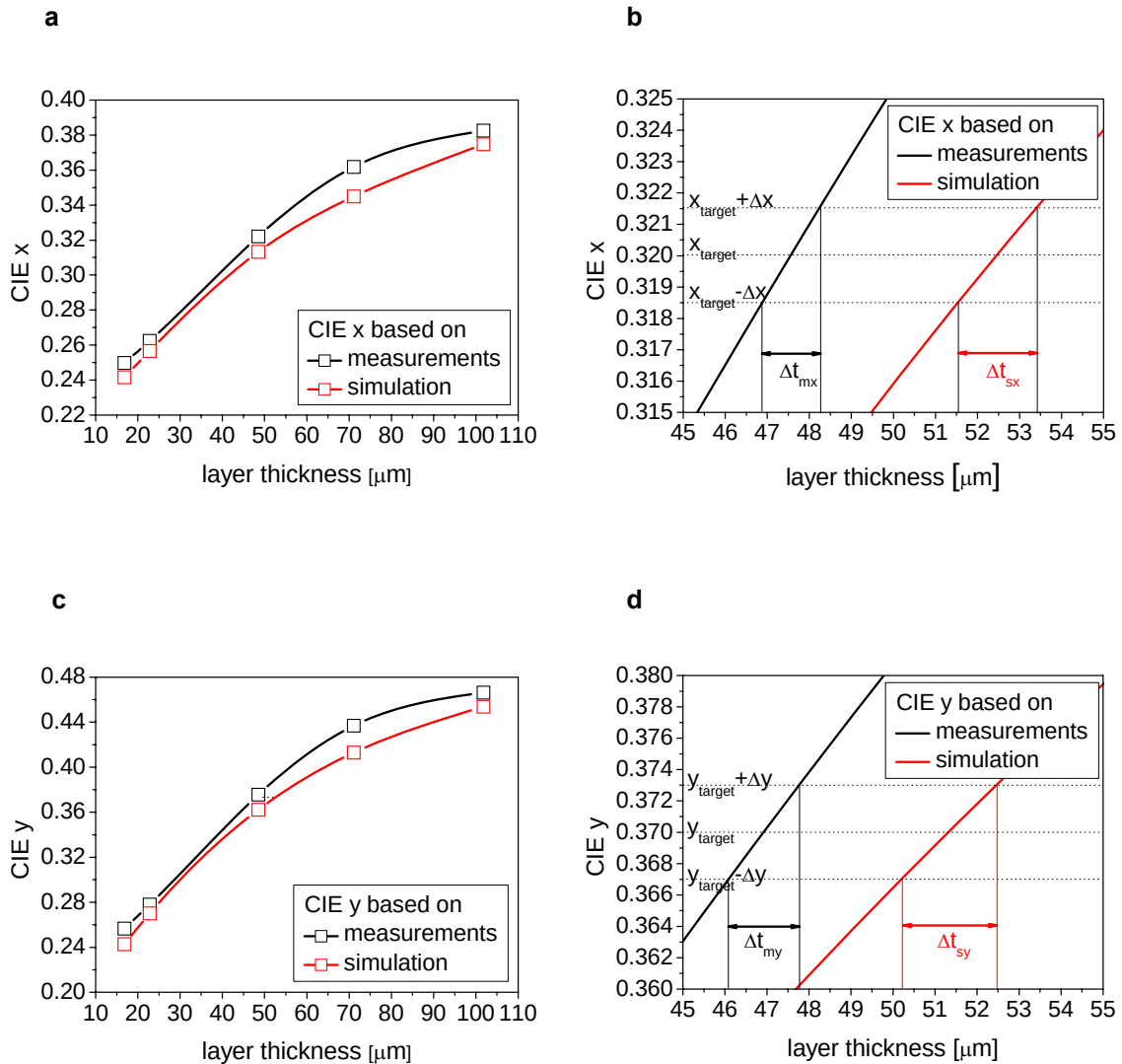


Fig. 5-15. CIE x and y coordinate as a function of layer thickness as obtained from measurements and simulations (a and c) for conversion layer set A. In the magnified plots (b) and (d) the derivation of the maximum allowable range of conversion layer thickness Δt for whitish target color coordinates in the range of $x_{target} = 0.32$ $y_{target} = 0.37$ is demonstrated.

Next, the output spectrum as a function of viewing angle is considered. The CIE-coordinates corresponding to the measured angular emission of the blue panel combined with layer A3 are shown in Fig. 5-16. A yellow shift in the light output is observed, when the viewing angle is increased. The corresponding simulation results (Fig. 5-16b) reproduce the same effect. This effect can be explained when considering photons which are generated by the OLED and coupled into the glass in different angles with respect to the substrate normal (Fig. 5-17). With increasing angle, the average optical path of a photon through the conversion layer into the ambient becomes longer, i.e. the probability of a photon being absorbed by the phosphor increases. Consequently, the probability of a photon leaving the conversion layer without being absorbed by the phosphor increases with decreasing propagation angle, which in turn leads to a more bluish emission at small viewing angles. This effect is scope of section 5.2.C, where an innovative approach to improve color homogeneity over the viewing angle is proposed.

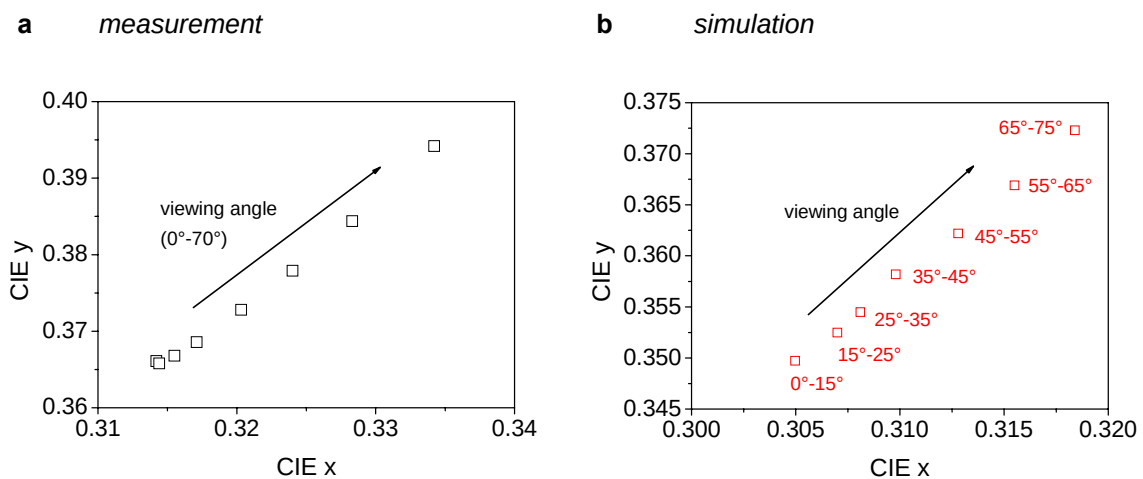


Fig. 5-16. Color coordinates of the light output as a function of viewing angle based on (a) measurement and (b) simulation for the blue panel equipped with down-conversion layer A3. The color coordinates in the graph of Figure (b) correspond to spectral distributions of simulated photons leaving the conversion layer in certain angular ranges with respect to the substrate normal.

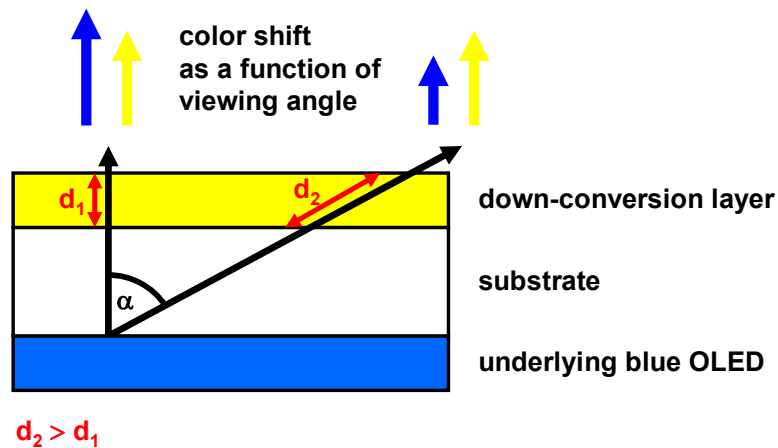


Fig. 5-17. The emission color of a typical down-conversion lighting device shows a yellow shift with increasing viewing angle. The color shift is due to the difference in the average optical path length through the conversion layer of photons coupled into the substrate in different angles.

Extraction Efficiency

After applying the down-conversion layer A3 atop the blue OLED panel, the device appeared not only white (CIE $x/y = 0.32/0.37$) but also much brighter. The luminous intensity measured in the direction of the substrate normal at 20 mA increased by a factor of 3.4 from 42 cd/m^2 to 141 cd/m^2 . This effect may be attributed to the higher sensitivity of the human eye at wavelengths related to yellow light than at wavelengths related to blue light (see chapter 2.3). The white spectrum (Fig. 5-18) has been fitted according to the simple down-conversion model proposed by Duggal *et al.* (see chapter 2.4.C). The fit allows the calculation of the conversion factor, which is the ratio of blue to expected white luminous efficiency. This calculation of the expected efficiency includes parameters related to the sensitivity of the human eye, the quantum yield of the phosphor and the Stokes shift between the energy of absorbed and re-emitted photons (see chapter 2.4). The conversion factor obtained by the fit is $c = 2.5$, far lower than the increase in luminous intensity by a factor of 3.4 seen experimentally. This difference should be attributed to light extraction enhancement due to light scattering by the phosphor particles, which is not considered by the model proposed by Duggal *et al.*.

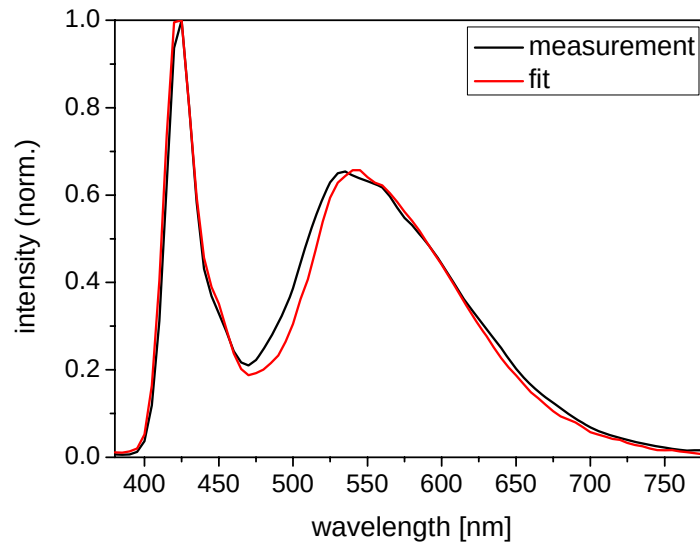


Fig. 5-18. Emission spectrum of the blue panel equipped with down-conversion layer A3 and its fit according to the model of Duggal et al..

The values of photon extraction efficiency η_{s-a} (definition see section 5.1.A) for the blue panel equipped with the different down-conversion layers used in this study were determined for a more detailed analysis of light outcoupling. In this consideration, the extraction efficiency η_{s-a} of the blue OLED panel without conversion layer is set to be equal to the one of the smaller 0.5 cm x 0.5 cm OLED which has the same structure as the panel regarding materials and layer thicknesses. Here, an extraction efficiency of $\eta_{s-a} = 0.44$ was derived by comparing the total light output obtained from the angular measurements of the emission with glass hemisphere to the one measured without glass hemisphere. Having in mind that the fraction of the generated photons coupled into the substrate, η_{OLED-s} , is not influenced by the down-conversion layer (i.e. $\eta_{OLED-s} = \text{constant}$), the extraction efficiency η_{s-a} for the blue panel equipped with a down-conversion layer can be derived from the measurements as follows:

$$(Eq. 5-5) \quad \eta_{ph}(blue) = \eta_{OLED-s} \eta_{s-a}(blue)$$

$$(Eq. 5-6) \quad \eta_{ph}(dc) = \eta_{OLED-s} \eta_{s-a}(dc)$$

$$(Eq. 5-7) \quad \rightarrow \quad \eta_{s-a}(dc) = \eta_{s-a}(blue) \frac{\eta_{ph}(dc)}{\eta_{ph}(blue)} = \eta_{s-a}(blue) \frac{O(dc)}{O(blue)},$$

where $\eta_{ph}(blue)$ is the total extraction efficiency of the blue panel (see Eq. 5-1),

$\eta_{s-a}(blue)$ is the fraction of photons coupled into the substrate of the blue panel, which is emitted into the ambient,

$\eta_{ph}(dc)$ is the total external efficiency of the blue panel equipped with the down-conversion layer,

$\eta_{s-a}(dc)$ is the fraction of photons coupled into the substrate, which is emitted through the substrate and the conversion layer into the ambient (converted and non-converted photons),

$O(blue)$ is the output of the blue panel (in photons) obtained from measurements of angular emission, and

$O(dc)$ is the output of the blue panel equipped with the conversion layer (in photons) obtained from measurements of angular emission.

Fig. 5-19a and Fig. 5-19b show the extraction efficiency versus the film thickness as determined, based on both measurements and simulations for both sets of down-conversion layers. In Fig. 19c the data are brought together into one graph by introducing the product of the layer thickness and the phosphor volume concentration, henceforth termed as *normalized layer thickness*, as magnitude for the axis of abscissae.

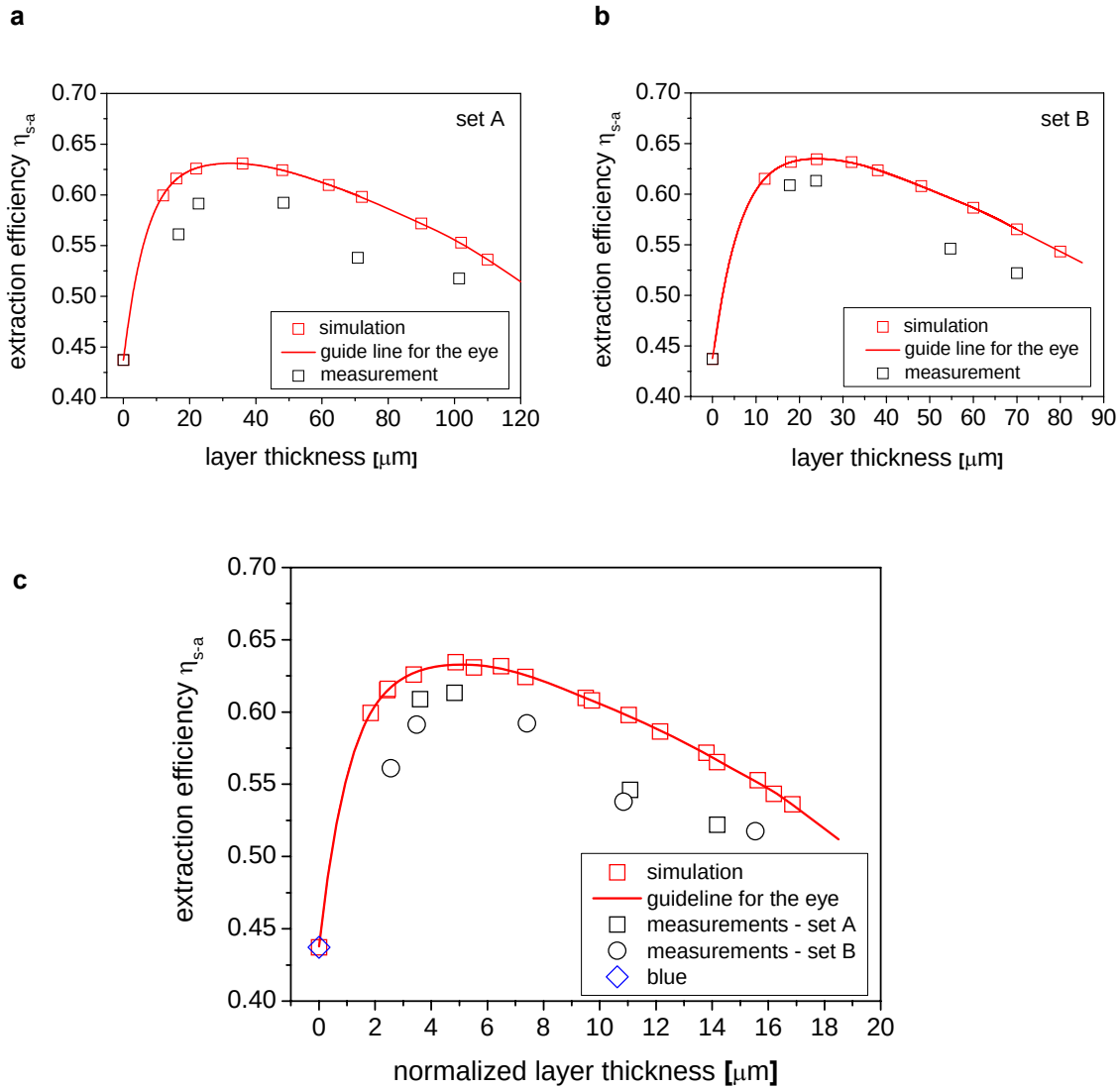


Fig. 5-19. Extraction efficiency as a function of layer thickness for the blue panel equipped with the layers of set A (a) and the layers of set B (b). The data for both sets are brought together into one graph by introducing the normalized layer thickness ¹² (c).

¹² Provided that absorption in the matrix material is negligible, the product of the layer thickness d and the phosphor volume concentration c will lead to an appropriate normalization, i.e. to a dimensionless description of the conversion layer, where the ratio $MFPW:d$ is constant for all pairs $c, d \in \{c, d \mid c \cdot d = d_{norm} = const\}$. This is obvious when contemplating Eq. 5-1:

$MFPW = 1 / (N \cdot q_{geo}) = V_p / (c \cdot q_{geo})$, where V_p is the average volume of one phosphor particle.

Considering two volume concentrations of the same phosphor powder (c_1, c_2), the corresponding layer

thicknesses d_1 and d_2 are related to the same normalized layer thickness: $c_1 \cdot d_1 = c_2 \cdot d_2 = d_{norm}$

$\rightarrow c_1 = d_{norm}/d_1, c_2 = d_{norm}/d_2$.

This translates into $MFPW_1 = (V_p \cdot d_1) / (d_{norm} \cdot q_{geo})$ and $MFPW_2 = (V_p \cdot d_2) / (d_{norm} \cdot q_{geo})$.

Here the constant ratio $MFPW:d$ is given by $MFPW_1/d_1 = MFPW_2/d_2 = V_p / (d_{norm} \cdot q_{geo})$.

The data presented in Fig. 5-19c can be described using a simple physical picture. In the plot based on measurements as well as in the plot based on simulation results, there is a value of normalized layer thickness related to a maximum in light extraction, which is 61 % as determined by measurements and 63 % in the simulations. At lower values, wave-guiding within the substrate is not efficiently suppressed by scattering at the phosphor particles (see Fig. 5-1, photon C), while at higher values, more and more light is back-scattered into the OLED stack leading to absorption losses (see Fig. 5-1, photon E). The peak value is the point where these two effects are balanced. Minor losses slightly increasing with layer thickness are caused by the finite quantum yield of the phosphor. There is good agreement between model prediction and experimental data, i.e. the slope of both plots is very similar and the location of the maximum in light extraction agrees. The extraction efficiencies predicted by simulation are slightly higher than the experimental data. These minor differences could be caused by setting the effective OLED reflectance, $R_{OLED}(\lambda)$, to be independent from the angle of incidence, which might lead to an overestimation of $R_{OLED}(\lambda)$ in the simulation (see chapter 5.1.B, section “Effective OLED Reflectance”). Furthermore, differences in the thicknesses of the active layers between the blue panel and the 0.5 cm x 0.5 cm OLED could lead to deviations in the location of the EMZ and, consequently, to deviations in the corresponding angular photon distributions $D(\alpha)$ (see chapter 2.2 and 4.2.B). This could be a reason for an error in the extraction efficiency $\eta_{s-a}(blue)$ assumed for the blue panel, which in turn could affect the extraction efficiencies determined according to Eq. 5-7.

5.2. Influences on Extraction Efficiency and Angular Color Homogeneity

In the previous sections, a model of a down-conversion OLED has been developed and experimentally confirmed. Some of the implications of this model for the performance of such devices are discussed in the following. In particular, it is analysed how the effective OLED reflectance and the phosphor particle size distribution influence extraction efficiency. Thereby, room for improvement and challenges in the design of down-conversion OLEDs are identified. Finally, an approach to improve color homogeneity over the viewing angle is demonstrated.

5.2.A Influence of OLED-Reflectance on Extraction Efficiency

Due to wave-guiding, back-scattering and isotropic re-emission from the excited phosphor, a fraction of the photons propagating in the down-conversion layer re-enter the active layers of the OLED, where photons can be either absorbed or reflected back into the down-conversion layer. Thus, the extraction efficiency of a down-conversion device relies on the effective reflectance of the underlying OLED. To analyse the impact of the OLED reflectance, the extraction efficiency as a function of R_{OLED} has been computed using the proposed ray-tracing model. Here the extraction efficiency of the blue OLED panel equipped with the conversion layer A3 was determined. In the simulation, the reflectance of the panel as a function of wavelength was replaced by values of R_{OLED} that were set to be independent from wavelength and varied from 0 to 1.

The extraction efficiency is plotted versus the effective reflectance of the OLED in Fig. 5-20. As the reflectance increases, the extraction efficiency also increases. At higher values of reflectance the slope of the plot becomes steeper. For a standard bottom emitting OLED, $R_{OLED} \approx 0.8$ is a typical value for the effective reflectance [Shia04a]. In this region, a change in reflectance of a few percent has a significant impact on extraction efficiency. This interrelationship should be kept in mind when choosing materials for OLED stacks, on whose substrate surface down-conversion layers or scattering layers for light extraction enhancement are applied. For example, in comparison to aluminum, silver has a higher reflectivity and its use as cathode material offers room for improvement in extraction efficiency. For high values of R_{OLED} , η_{s-a} can be nearly unity, i.e. very efficient “photon recycling” occurs. Intuitively,

this is expected since, in the absence of absorption losses in the active layers, a given photon can impinge upon the interface many times until it escapes.

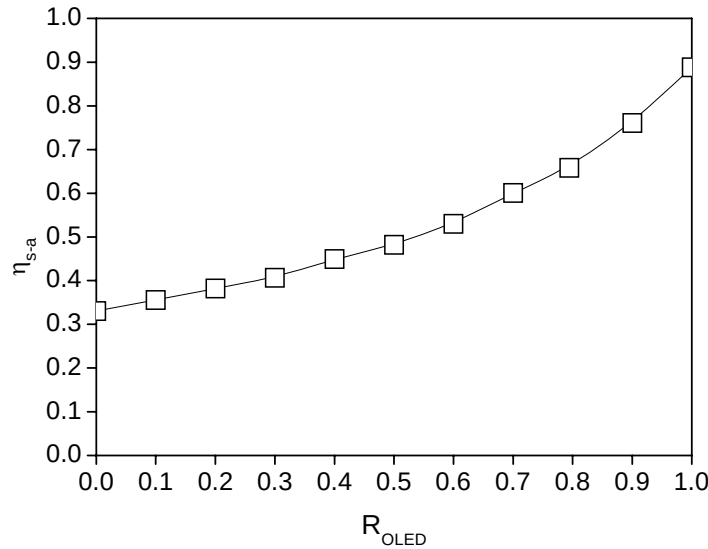


Fig. 5-20. Extraction efficiency as a function of effective OLED reflectance obtained by ray-tracing simulation.

As a result of the simulations mentioned above, the color coordinates related to the integrated spectra are given in Fig. 5-21. As the reflectance increases, the color of device emission is shifted from bluish white to greenish/yellowish white. This effect can be explained by considering the isotropic re-emission of the phosphor. Half of the converted photons (related to wavelengths in the yellow range of the visible spectrum) are re-emitted towards the OLED stack where the absorption losses occur. However, at higher values of reflectivity, the probability of photons being reflected into the conversion-layer and being extracted into air increases. Consequently, the emission color of a down-conversion OLED is not only determined by the thickness of the down-conversion layer but also by the effective device reflectance, i.e. when applying similar down-conversion layers on two OLEDs with the same spectral distribution of emission, the resulting output spectra may vary if the stacks differ in reflectance.

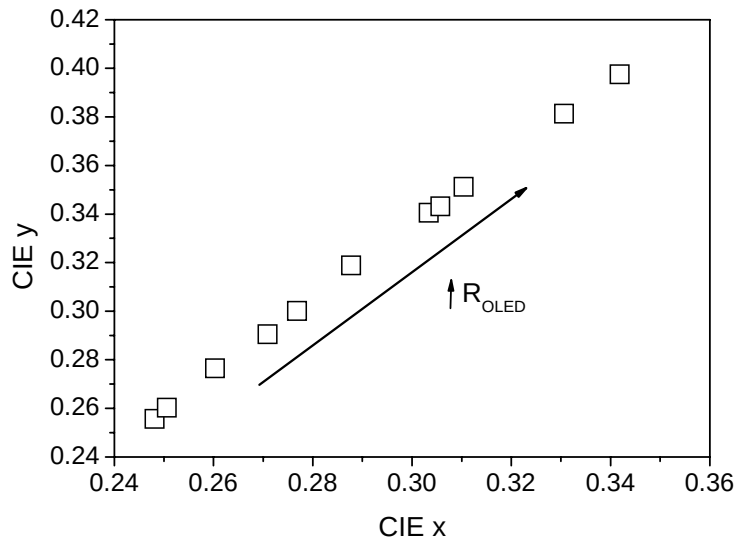


Fig. 5-21. CIE-coordinates related to the emission of the simulated down-conversion device as a function of OLED reflectance.

5.2.B Role of the Phosphor Particle Size Distribution

In the presented ray-tracing model, the behaviour of photons impinging particles in the down-conversion layer is given by the average single scattering/absorption characteristics. These characteristics are determined by the particle size distribution of the phosphor powder. In contrast to the analysis of extraction efficiency as a function of effective OLED reflectance, the complex influence of the average single scattering/absorption characteristics on resulting device efficiency of down-conversion OLEDs can hardly be estimated without modelling.

To investigate the effect of phosphor particle size distribution on extraction efficiency, four distributions of YAG:Ce³⁺ particle size ($\nu_1(D)$, $\nu_2(D)$, $\nu_3(D)$, $\nu_4(D)$) and their corresponding average single scattering/absorption characteristics are analysed. Distributions as $\nu_1(D)$ and $\nu_3(D)$ can be obtained by the technical phosphor-annealing process and subsequent milling of the powder [Berb06]. Here $\nu_3(D)$ is the particle size distribution of the phosphor powder used in the experiments presented in chapter 5.1. The distributions $\nu_2(D)$ and $\nu_4(D)$ are derivatives of $\nu_1(D)$ and $\nu_3(D)$, respectively, and represent powders as they would be received from an ideal classification process: Distribution $\nu_2(D)$ was derived by removing all particles smaller than a certain diameter D_1 from distribution $\nu_1(D)$; distribution $\nu_4(D)$, accordingly, was derived by removing all particles smaller than a certain diameter D_2

from distribution $\nu_3(D)$. The average particle size increases from distribution $\nu_1(D)$ to distribution $\nu_4(D)$.

For each of the distributions $\nu_1(D)$, $\nu_2(D)$, $\nu_4(D)$, the average single scattering/absorption characteristics in the silicone used for the down-conversion layers (see chapter 5.1) as surrounding medium were computed according to MIE-theory. As a result of this computation, Fig. 5-22 summarizes the absorption probability at wavelength 460 nm. The scattering functions associated to the distributions are plotted in Fig. 5-23 a-d exemplarily for wavelengths 420 nm, 530 nm, and 600 nm (the corresponding logarithmic plots are given in Fig. E-1 in the appendix).

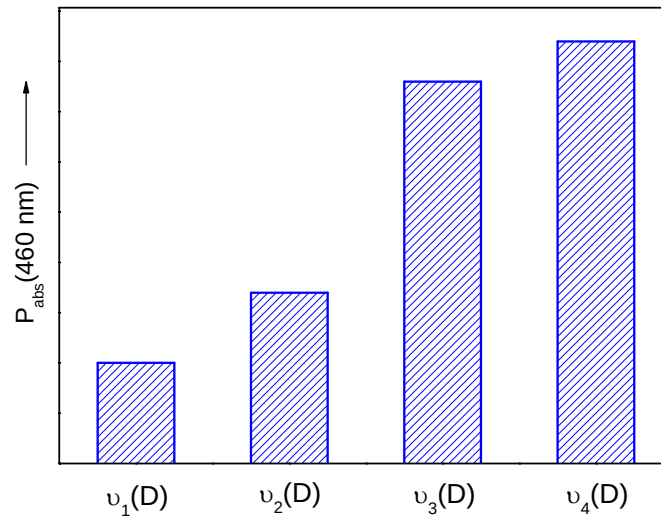


Fig. 5-22. Absorption probability at wavelength 460 nm for the four considered distributions of phosphor particle size (surrounding medium: silicone).

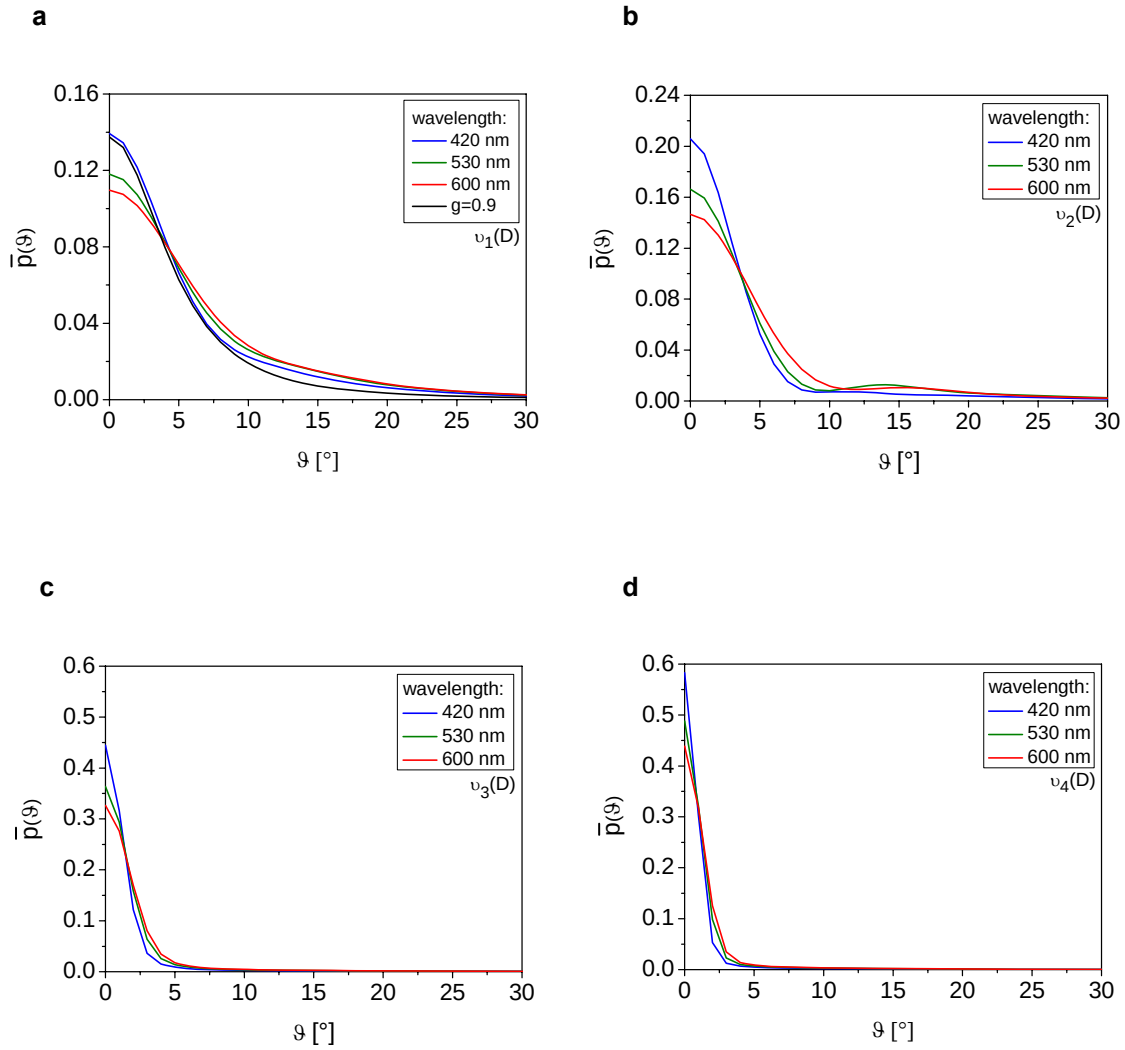


Fig. 5-23. Linear plots of the scattering functions in silicone corresponding to the YAG:Ce³⁺ phosphor particle size distributions $\nu_1(D)$, $\nu_2(D)$, $\nu_3(D)$, $\nu_4(D)$ (derived according to Mie-theory). In (a) the Henyey-Greenstein function related to $g = 0.9$ is plotted (black line).

As already performed in the case of distribution $\nu_3(D)$, the extraction efficiency as a function of normalized layer thickness was simulated for devices which comprise the blue PLED panel and down-conversion layers containing YAG:Ce³⁺ powders with particle size distributions $\nu_1(D)$, $\nu_2(D)$, $\nu_4(D)$. Here, in the ray-tracing simulation, the model inputs characterizing the underlying OLED were the same as used in chapter 5.1.C. The results are depicted in Fig. 5-24. Additionally, the dependence of extraction efficiency on normalized layer thickness for the case of the distribution $\nu_3(D)$ is plotted in Fig. 5-24, which has already been presented in chapter 5.1.C.

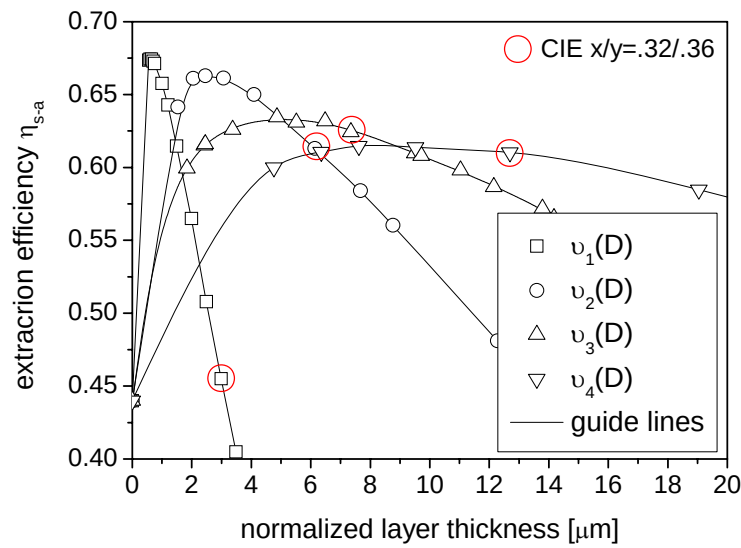


Fig. 5-24. Extraction efficiency η_{s-a} as a function of normalized layer thickness, which has been obtained by simulation for each of the considered phosphor particle size distributions. All data points related to similar color coordinates (CIE $x/y \approx 0.32/0.38$) are marked with a circle.

For each particle size distribution, the computed extraction efficiency η_{s-a} , as a function of layer thickness, has the same characteristic slope already discussed in chapter 5.1.C, i.e. initially η_{s-a} increases as the layer thickness is increased, then η_{s-a} reaches a maximum value and decreases as the layer thickness is further increased. With increasing average particle size the corresponding peak value decreases from 0.67 to 0.61.

The computed dependence of the extraction efficiency on particle size and on normalized layer thickness, respectively, is related to results published by Bathelt *et al.* [Bath07], [Gärd05]. They investigated light extraction enhancement by volumetric light scattering in diffuse layers applied on the substrate surface. The diffuse layers comprised hollow polymer particles embedded in a transparent acrylate matrix. Bathelt *et al.* developed a ray-tracing model that quantifies the effect of light scattering on the output of bottom emitting OLEDs. In this model, the scattering function of the particles embedded in the diffuse layer is given by the Henyey-Greenstein scattering function. Here the effect of the particle size is contained in a single parameter g (see appendix D). This parameter g is the expectation value of the cosines of the scattering angle. Analogous to the data shown in Fig. 5-24 for each value of g , their model predicted a maximum in light extraction enhancement at a particular value of particle loading at a fixed layer thickness. The maximum enhancement ($a = 1.4$) was reached for particles related to g -factors in the range between 0.5 and 0.7. Higher and lower values of

g led to less effective light extraction enhancement. Comparing the plot of the Henyey-Greenstein function to the average scattering functions corresponding to the four phosphor particle size distributions introduced above, each of the four scattering functions would be related to a g -factor $\geq \approx 0.9$ (see appendix Fig. D-1 and Fig. 5-23). However, the deviation of scattered light from its original trajectory is more and more pronounced from distribution $\nu_4(D)$ to $\nu_1(D)$. Hence, the scattering function corresponding to distribution $\nu_1(D)$, for which the simulation predicts the highest extraction efficiency, is closest to the optimum scattering function proposed by Bathelt *et al.* for light extraction enhancement by diffuse layers.

Though there is similarity between the results of the analysis of light extraction enhancement by Bathelt *et al.* and the predictions of the model proposed within this work (i.e. similar curve progression of the extraction efficiency as a function of layer thickness/scatterance and same magnitude of order in reachable light extraction enhancement), major differences between both studies exist regarding the physical processes within the layers and the purpose of the considered substrate surface modifications: First of all, while in an ideal diffuse layer photons are only scattered by the embedded particles, in a down-conversion layer a fraction of the photons also undergoes *absorption and isotropic re-emission*. Furthermore, the primary purpose of a phosphor layer is the color conversion from blue to white. This leads to major challenges in translating the guidelines for efficiency enhancement published by Bathelt *et al.* to a down-conversion OLED. To illustrate this, values of η_{s-a} related to similar color coordinates in the white region (CIE $x/y = .32/.38$) are marked with a circle in each curve of Fig. 5-24. Consequently, in this case the phosphor particle distribution $\nu_3(D)$ is most suitable for the efficient generation of white light. Here, according to simulation, an extraction efficiency of $\eta_{s-a} = 0.67$ can be reached, which was almost reached experimentally as shown in chapter 5.1.C (see Fig. 5-19). While the extraction efficiencies related to $\nu_2(D)$ and $\nu_4(D)$ are in the same magnitude of order as the one corresponding to $\nu_3(D)$, the use of distribution $\nu_1(D)$ would lead to a white emitting device of significantly lower efficiency.

When optimizing diffuse layers for light extraction enhancement, there is complete freedom in the choice of appropriate layer parameters (layer thickness, particle loading and particle size). However, the optimization of down-conversion layers is restricted by the target color coordinates. In the optimum configuration, the fraction of photons, which is necessary to reach the target color coordinates, is converted by the layer and at the same scattering at the phosphor particles leads to efficient light extraction enhancement. For given target color coordinates, this balance is determined by the ratio between scattering and absorption within

the layer, i.e. in terms of the ray-tracing model by the absorption probability (Fig. 5-22). The average absorption cross section and the average scattering cross section related to a given phosphor powder are magnitudes which are not only determined by the particle size distribution, but also by the complex refractive index of the phosphor material and by the refractive index of the surrounding matrix material (see chapter 2.5). Considering these circumstances, it seems hardly possible to develop general design guide-lines for the optimum phosphor particle size (distribution). However, the presented results implicate a careful choice of the phosphor powder, since the particle size distribution has a significant impact on the resulting external device efficiency of white light-emitting down-conversion OLEDs.

Additionally, the use of nanoparticles [Sand03], of molecular dyes (for example perylene [Schl97]) or of polymers ([Hide97], [Zhan98]) as luminescence converting materials is discussed. The small size of these materials – significantly smaller than the wavelength of visible light – eliminates all light scattering. In LED technology, quantum dots are regarded as potential phosphors leading to an increase of device efficiency. According to reference [Sand03], the introduction of quantum dots could double external device efficiency in comparison to white LEDs based on conventional larger size phosphor powders which cause optical back scattering losses.

Contemplating a non-scattering phosphor, the only change in the propagation direction of light within the down-conversion layer is given by isotropic re-emission of the phosphor. Assuming a refractive index of $n_{matrix} = 1.5$ for the matrix material, the critical angle for total internal reflection at the interface to air is $\alpha_{crit} = \sin^{-1}(1/n_{matrix}) \approx 42^\circ$. Derived from geometrical considerations¹³, the fraction of re-emission within the escape cone in the direction towards the interface to air is given by:

$$(Eq. 5-8) \quad P_1 = \frac{1}{2}(1 - \cos \alpha_{crit}) \approx 0.13 \quad \text{for } \alpha_{crit} = 42^\circ.$$

Furthermore, light is re-emitted towards the OLED stack. The major part of the light incidence at the cathode is reflected back. Thus another fraction of the phosphor re-emission, P_2 , is extracted to air:

$$(Eq. 5-9) \quad P_2 = R_{OLED} \cdot P_1$$

¹³ Eq. 5-8 expresses the ratio between a spherical sector with an apex angle of $2\alpha_{crit}$ to the total sphere volume.

The effective OLED stack reflectance of a typical bottom emitting OLED is $R_{OLED} \approx 0.8$ (i.e. $P_2 \approx 0.1$). Hence, $P_1 + P_2 \approx 0.23$ corresponds to the extraction efficiency η_{s-a} for the converted light. For comparison, the typical outcoupling efficiency from glass to air is $\eta_{s-a} \approx 0.5$ for an optimized conventional bottom emitting OLED with one emissive component (no substrate surface modification) [Lu02]. Contemplating that the non-absorbed fraction of the blue OLED emission is not influenced by the phosphor, the external device efficiency is significantly reduced in comparison to the unmodified blue OLED.

Considering light extraction from a flat panel down-conversion OLED, the introduction of non-scattering phosphors is disadvantageous. However, if a reflecting off-state appearance of the device is desired, the use of non-scattering phosphors is indispensable. Scattering particles of a material non-absorbing in the wavelength region of visible light (Al_2O_3 for example) might be added, if a non-scattering phosphor is needed to obtain the output spectrum aimed at.

5.2.C Reduction of the Dependence of Emission Color on Viewing Angle using Half-Cavity Effect

Considering the emission color of a typical white-emitting down-conversion device, a yellow shift in the light output is observed, when the viewing angle is increased (see chapter 5.1.C). This effect can be explained when considering photons, which are generated by the underlying (blue) light source and coupled into the down-conversion layer in different angles with respect to the substrate normal (Fig. 5-17). With increasing in-coupling angle, the average optical path of a photon through the conversion layer into the ambient becomes longer, i.e. the probability of a photon being absorbed by the phosphor increases. Consequently, the probability of a photon leaving the conversion layer without being absorbed increases with decreasing propagation angle. Furthermore, a typical OLED is optimized in such a way, that the emission is directed into a preferably small range of solid angle in order to minimize losses due to total internal reflection at the interface between glass and air. This typical angular distribution of emission (which is related to the in-coupling angle into the down-conversion layer) and the dependence of phosphor absorption probability on the in-coupling angle lead to a more bluish emission at smaller viewing angles.

An approach to reduce the dependence of emission color on viewing angle is illustrated in the following. This novel approach is based on the enhancement of the blue emission into the down-conversion layer at higher angles, i.e. the main direction of emission

differs significantly from the substrate normal. The enhancement of blue emission at higher angles acts against the increasing probability of a photon being absorbed by the phosphor at higher emission angles. The feasibility of the proposed approach is demonstrated by a study based on a series of blue emitting fluorescent sm-LEDs equipped with a down-conversion layer. In the optical half-cavity of the devices, the distance between the EML and the reflecting cathode was varied in order to obtain different angular distributions of emission within the substrate (see chapter 2.2 and 4). Here the refractive index of the substrate glass matched the refractive index of the matrix of the conversion layer. Thus, the angular distribution of emission within the substrate corresponded to the emission into the down-conversion layer as a function of angle.

Blue sm-OLEDs and Down-Conversion Layer

The structure of the blue sm-LEDs used for this study was 130 nm ITO / 20 nm HTL / 10 nm electron blocking layer (EBL)¹⁴ / 25 nm EML / 10 nm hole blocking layer (HBL) / ETL / 150 nm Ag. The thickness of the ETL (15 nm, 30 nm, 50 nm) was changed in order to vary the angular distribution of emission within the substrate. The architecture of these diodes is shown in Fig. 5-25. Additionally, the table in Fig. 5-25 contains the device nomenclature based on the thickness of the ETL. The peak wavelength of the fluorescent blue emitting dye in the EML was ≈ 460 nm. The ETL and HTL were doped by materials improving electron and hole transport respectively (*n-/p-doping*). The diodes were fabricated as follows: The organic stack was applied on ITO coated substrates by standard evaporation technique from crucibles. Thereby the evaporation rate was 1 Å/s at a base pressure of 10^{-7} mbar. Following evaporation of the Ag cathode, the devices were encapsulated with a glass lid and getter. The ETL and its dopant, the HTL and its dopant, and the matrix of the EML and its blue dye were applied by co-evaporation. Both diodes with 4 mm² active area and diodes with 200 mm² active area were fabricated for each ETL layer thickness.

¹⁴ The HBL consists of a mainly electron-transporting material and EBL consists of a mainly hole-transporting material. By incorporating a HBL and an EBL into the device, the recombination of charge carriers within the EML is enhanced.

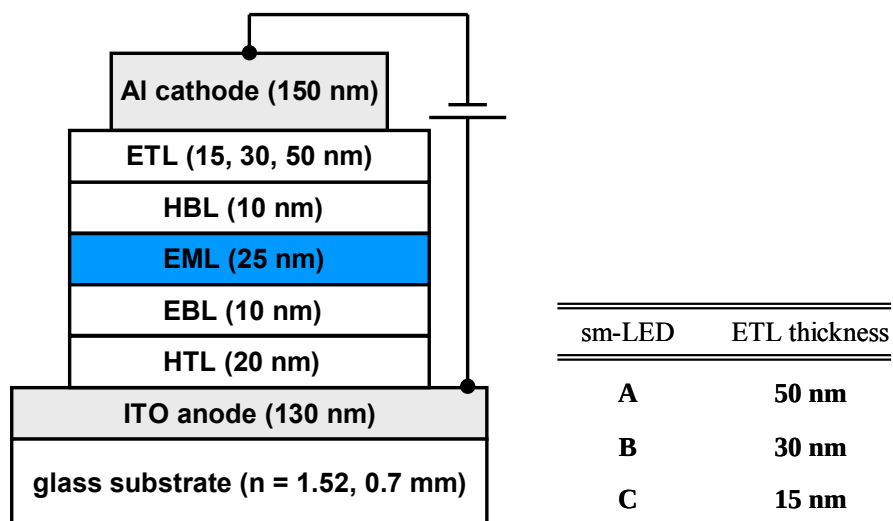


Fig. 5-25. Structure of the devices used in this study.

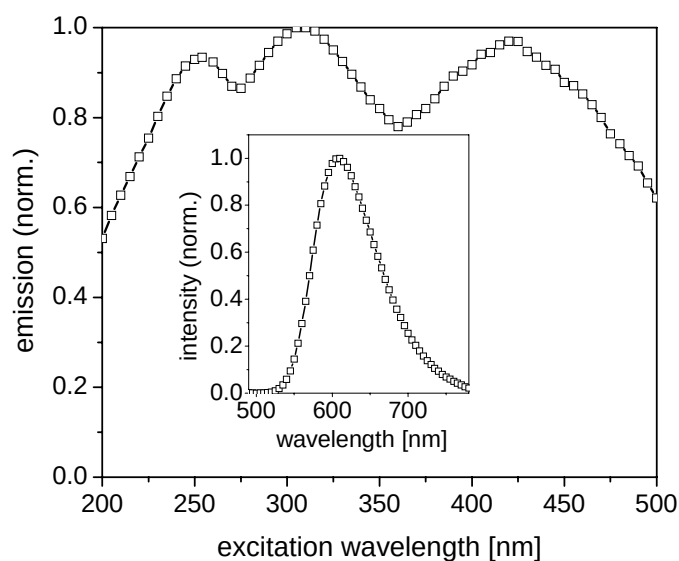


Fig. 5-26. Excitation spectrum of OSRAM nitridosilicate phosphor (re-emission measured at 610 nm). The inset shows the phosphor re-emission spectrum (excitation wavelength 460 nm). The data has been obtained from OSRAM GmbH.

The down-conversion layer contained YAG:Ce^{3+} and an orange nitridosilicate phosphor. The YAG:Ce^{3+} -powder corresponds to the phosphor which was used in the experiments described in chapter 5.1. Fig. 5-26 shows the excitation spectrum and the emission spectrum of the orange nitridosilicate phosphor ($[\text{Sr,Ba,Ca}]_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$) offering a

quantum yield of about 90 % of typical YAG:Ce³⁺ (phosphor data has been obtained from OSRAM GmbH [Berb06]). The material is an internal product of OSRAM GmbH [Jerm04], [Euro05]. By means of both a two axis rotary high-speed mixer and a masticator, the phosphor particles were thoroughly dispersed in an epoxy resin (refractive index 1.52). This mixture (3 vol% YAG:Ce³⁺, 27 vol% nitridosilicate, 70 vol% epoxy) was then applied on a free-standing glass substrate by means of screen printing. This film was cured 3 h at 160 °C. The thickness of the cured film was 15 µm. The refractive index of the substrate glass ($n = 1.52$) matches the refractive index of the matrix of the down-conversion layer. Thus, the angular distribution of emission within the substrate corresponds to the in-coupling angle into the down-conversion layer as a function of angle.

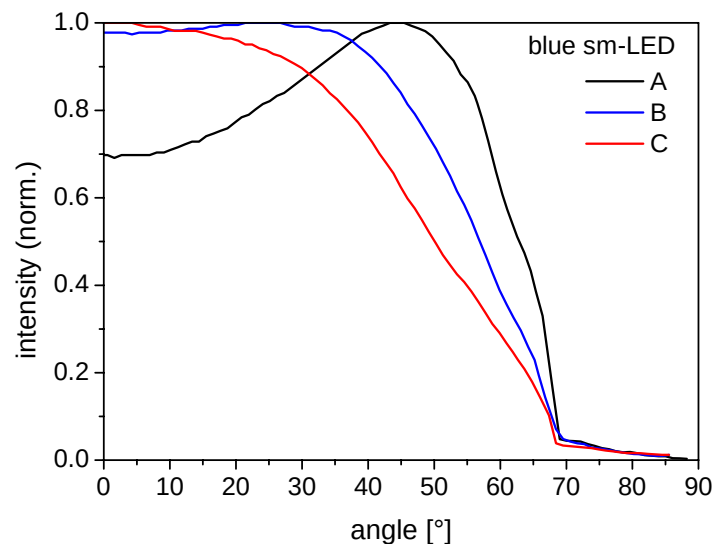


Fig. 5-27. The angular distribution of emission within the substrate of the three blue sm-LEDs as measured using a glass hemisphere coupled to the substrate surface of the 4 mm² active area diodes (operation current density 7 mA/cm²).

Results and Discussion

Fig. 5-27 shows the angular distribution of emission within the substrate for all three types of sm-LEDs, A, B and C (without down-conversion layer). The emission within the substrate was measured by means of a glass hemisphere optically coupled to the small 4 mm² diodes (the method of measurement is described in chapter 5.1.B). Here the emission was measured from the hemisphere, using a fiber spectrometer Instrument Systems CAS 140B. The emission is more and more opened out towards higher angles, when the thickness of the

ETL is increased, i.e. when the distance between the emission zone and the reflecting metal cathode is increased within the optical half-cavity formed by the devices.

Additionally, the total light output of the 4 mm² diodes has been measured in an integrating sphere. The measurements were performed with and without glass hemisphere optically coupled to the substrate surface. This way, the external light output of the diodes into the ambient (measurement without hemisphere) and the total emission into the substrate (measurement with hemisphere) were measured at a fixed current density of 7 mA/cm². The ratio between both values corresponds to the extraction efficiency η_{s-a} (definition see chapter 4.2.B). From sm-LED C to A, η_{s-a} decreases (see Table 5-2). This is a result of the shift of the emission within the substrate to higher angles from sm-LED C to A, which leads to an increase of the fraction of substrate wave-guided light (see chapter 4.2.B). Additionally, Table 5-2 lists the CIE-coordinates detected in the integrating sphere when the diodes were equipped with the glass hemisphere. A green shift in integrated emission color was observed from C to A. This can also be attributed to optical half-cavity effects: An increase of the optical half-cavity length causes the accentuation of emission at higher wavelengths, which in turn leads to emission related to a higher CIE y-coordinate.

Table 5-2. Ratio between sm-LED emission with and without glass hemisphere as obtained from the measurements in the integrating sphere. Additionally, the CIE x/y coordinates corresponding to the emission with glass hemisphere are listed.

sm-LED	ratio between light output with and without glass hemisphere ($=\eta_{s-a}$)	CIE x/y with glass hemisphere
A	0.43	.153 / .227
B	0.51	.147 / .200
C	0.56	.146 / .184

Next, the blue sm-LEDs were equipped with the down-conversion layer. Therefore the substrate surfaces of the 200 mm² sm-OLEDs were optically coupled to the free-standing glass substrates carrying the down-conversion layer. Now the device emission as a function of viewing angle was measured at a current density of 7 mA/cm², using a standard goniometer (detector: Instrument Systems CAS 140B). Fig. 5-28 shows the CIE color coordinates as a function of viewing angle, which were derived from the measurements. From device C to A,

the dependence of emission color on viewing angle is significantly reduced: The shift in the CIE x-coordinate as a function of viewing angle is decreased by $\approx 50\%$. The CIE x/y plots corresponding to the different devices are y-shifted at the same time. This can be explained by the variance in CIE y-coordinate corresponding to the emission of the different underlying blue sm-LEDs, which has already been demonstrated above. The improved homogeneity of emission color over the viewing angle is also reflected in the graphs of Fig. 5-29. Here the emission spectrum in the direction of the substrate normal and the spectrum related to a viewing angle of 70° are plotted for the down-conversion devices with underlying sm-LEDs A and C. Comparing both devices, the spectrum at the angle of 70° differs significantly less from the spectrum in front direction in the case of sm-LED A.

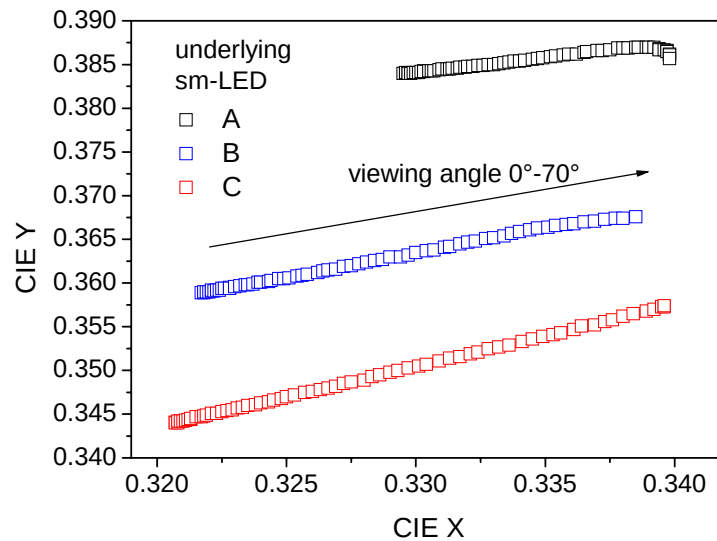


Fig. 5-28. CIE x/y coordinates as a function of viewing angle for the three blue sm-LEDs equipped with the down-conversion layers. The dependence of emission color on the viewing angle is significantly reduced from sm-LED C to A.

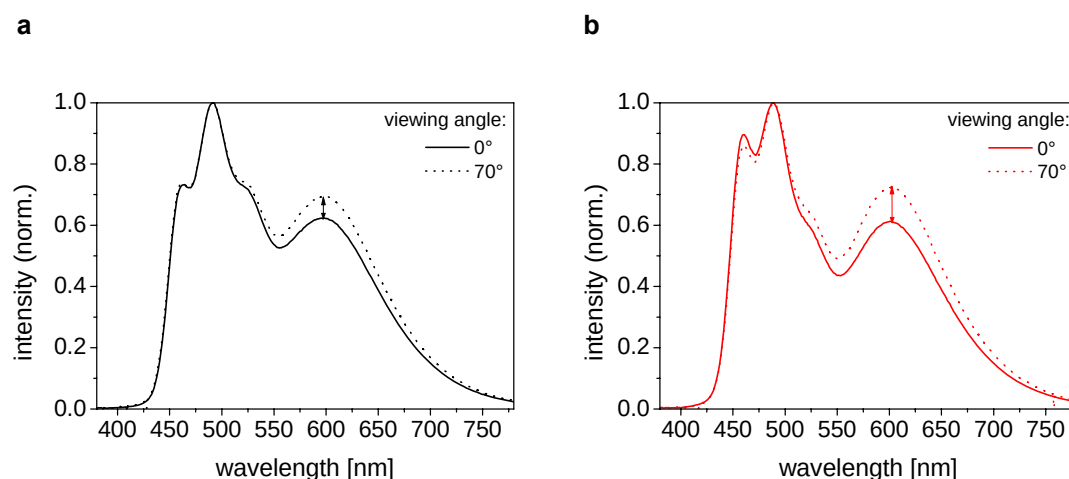


Fig. 5-29. Spectra of the sm-LEDs A (a) and C (b), which were equipped with the down-conversion layer. The spectra were measured in the direction of the substrate normal and at a viewing angle of 70°. Comparing sm-LED C to A, the dependence of the spectrum on the viewing angle is significantly reduced.

Table 5-3. Total light output before and after applying the down-conversion layer. Additionally, the apparent light extraction enhancement, due to the down-conversion layer, and the calculated extraction efficiency η_{s-a} are listed.

sm-LED	light output without conversion layer (arbitrary units)	light output with conversion layer (arbitrary units)	apparent enhancement	η_{s-a}
A	0.089	0.111	1.25	0.54
B	0.097	0.106	1.10	0.56
C	0.106	0.107	1.01	0.56

Now the external efficiency of the down-conversion devices is considered. Light scattering due to phosphor particles embedded in a conversion layer on the substrate surface of an OLED has been reported to enhance light extraction ([Dugg02] and chapter 5.1.C). In order to take changes in light extraction into account, the total radiative light output of the blue sm-LEDs with and without down-conversion layer has been determined (see Table 5-3). The values were derived by integration of the measurements, using the goniometer setup over the whole half-space of emission. The apparent light extraction enhancement due to the phosphor layer shows a dependence on device structure, i.e. a dependence on the thickness of

the ETL. However, the resultant external light output is approximately constant for the three sm-LEDs, when applying the down-conversion layer on the substrate surface. Considering the measurements with the glass hemisphere and the goniometer measurements of the light output from the devices equipped with down-conversion layer, the efficiency of light extraction from the down-conversion to the ambient (i.e. η_{s-a}) can be derived. The values of η_{s-a} are approximately equal for the three devices. This independence of extraction efficiency η_{s-a} from the angular distribution of emission within the substrate compares favourably to the study of light extraction enhancement due to substrate surface modification, which has been presented in chapter 4. The blue sm-LED A leads to the best color homogeneity without losses in external device efficiency, even though its extraction efficiency η_{s-a} without conversion-layer is significantly lower in comparison to the diodes B and C.

In conclusion, the feasibility of the proposed approach to reduce the dependence of emission color on viewing angle for down-conversion OLEDs has been shown. The enhancement of blue emission at higher angles acted against the increasing probability of a photon being absorbed by the conversion layer at higher emission angles successfully. The homogeneity of emission color over the viewing angle has been improved without affecting external device efficiency of the resulting down-conversion OLED.

5.3. Outlook: Realization of the Down-Conversion Approach in OLED Lighting Applications

For illumination applications, the color of light emission needs to be equivalent to that of a blackbody source (Planckian locus, see chapter 2.3.C) between 3000 and 6000 K. Thereby, the allowable colors in terms of the CIE x - and y -coordinates fall within 0.01 x or y units of the exact blackbody source color [Wysz00]. Finding appropriate luminescence converting materials for devices with underlying blue OLED characteristics is much more challenging than in the case of white emitting devices based on inorganic LEDs, since organic EL-spectra are significantly broader than EL-spectra of classical blue inorganic LEDs. For example, in most cases it is not possible to reach the Planckian locus by applying standard YAG:Ce³⁺ phosphor on a blue OLED [Klein07]. More reddish phosphorescing converters have to be introduced such as nitridosilicate phosphors to overcome this limitation.

Furthermore, the use of phosphor mixtures or down-conversion systems comprising several phosphor layers offer more freedom in creating individual colors of device emission. This is demonstrated in Fig. 5-30, where the emission spectra of a cold and a warm white emitting down-conversion OLED is shown. The corresponding color coordinates (CIE $x/y = 0.33/0.33$ for the cold white and CIE $x/y = 0.37/0.37$ for the warm white) are equivalent to the Planckian locus. The spectra are calculated using the down-conversion model presented by Duggal *et al.* (see chapter 3.4). Both spectra are based on the same blue light source, which corresponds to a typical deep blue emitting PLED (peak wavelength 455 nm, [Dugg02]), and the same down-conversion system, which comprises a YAG:Ce³⁺ layer and an OSRAM nitridosilicate phosphor layer (excitation and re-emission spectra of nitridosilicate phosphor are given in section 5.2.C). Thus, by varying the effective absorption length of the phosphor layers, a variety of emission color can be generated using the same blue OLED.

Contemplating the ratio of blue to expected white photometric efficiency, conversion factors of $c = 2.43$ for the warm white and of $c = 2.36$ for the cold white have been determined according to Eq. 2-23. Based on literature, present deep blue emitting fluorescent sm-LEDs and PLEDs offer luminous efficiencies in the range of 3 cd/A and power efficiencies in the range of 1.5 lm/W (see chapter 3.1). This translates into an expected luminous efficiency of 7 cd/A and an expected power efficiency of 3.5 lm/W for white emission (in this estimation light extraction enhancement due to scattering within the down-conversion layer is not considered, see definition of the conversion factor in chapter 2.4.C). When comparing the expected efficiency of white light-emitting down-conversion devices

based on deep blue emitting fluorescent OLEDs to the power efficiency of a typical incandescent lamp (13-20 lm/W [OIDA02]), it becomes obvious that there is need of more efficient blue PHOLEDs for the further development of the down-conversion approach.

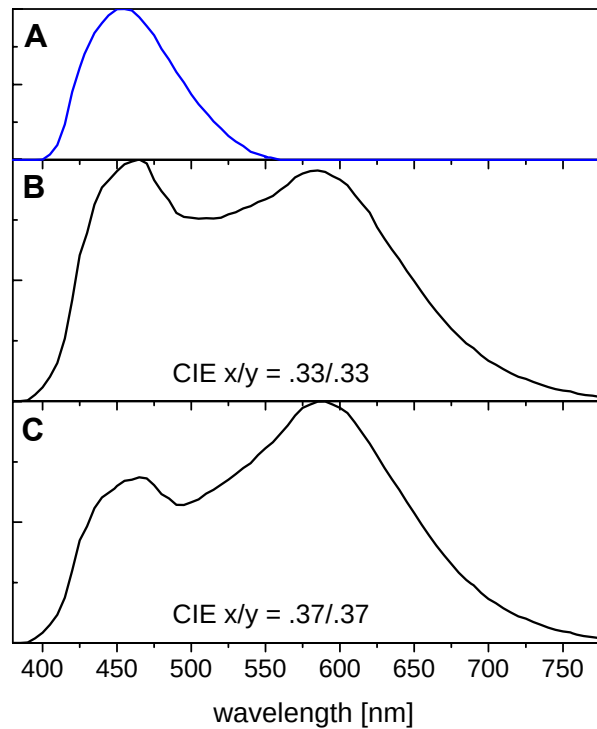


Fig. 5-30. Generation of cold (B) and warm (C) white based on a typical deep blue emitting OLED (A), using the same phosphor down-conversion system (YAG:Ce³⁺ layer and OSRAM nitridosilicate phosphor layer). The white spectra are calculated according to the down-conversion model proposed by Duggal et al. [Dugg02].

To show the feasibility of a highly efficient white emitting device with underlying blue PHOLED, a phosphor layer was applied to the outside surface of a 14 mm x 14 mm blue PHOLED with the same architecture as the device presented in chapter 3.2 (device D) [Krum06b]. The down-conversion layer contained OSRAM nitridosilicate phosphor. Using a masticator, the phosphor particles were thoroughly dispersed in a silicone matrix (refractive index 1.47). This mixture was then applied onto the substrate, using the doctor blade technique. The down-conversion layer was cured at 70 °C for 24 h. The thickness of the cured layer was 90 µm as measured by profilometry.

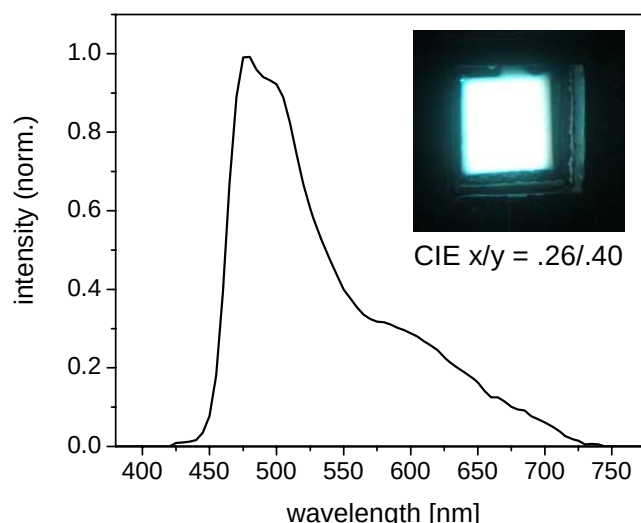


Fig. 5-31. Emission spectrum of a highly efficient white light-emitting device. The underlying blue PHOLED emission is down-converted by OSRAM nitridosilicate phosphor. The picture shows the white light-emitting device in operation.

The photo in Fig. 5-31 shows the white light source developed by down-converting the blue PHOLED with the nitridosilicate phosphor. The graph in Fig. 5-31 shows the normalized output spectrum of the device. The corresponding color coordinates of this white light source were CIE $x/y = 0.26/0.40$. By down-converting a blue PHOLED with efficiencies of 14 lm/W and 22 cd/A with a nitridosilicate phosphor, a highly efficient white light-emitting source with power efficiency of 25 lm/W at luminous efficiency reaching 39 cd/A was obtained.

To achieve *illumination quality white*, i.e. warm white emission corresponding to color coordinates on the Planckian locus, novel reddish phosphors are needed for down-converting sky-blue PHOLED emission¹⁵. For this purpose, the ideal phosphor would mainly absorb at wavelengths in the green range of the visible spectrum. This way the dominance wavelength of the non absorbed fraction of the blue emission is shifted to shorter wavelengths, leading to resultant white emission related to a lower CIE y -coordinate (i.e. reduction of the greenish fraction of the light emitted by the underlying sky-blue PHOLED). Fig. 5-32 illustrates the generation of white light by down-converting sky-blue PHOLED emission,

¹⁵ Though deeply blue organic electrophosphorescence is focus of current research [Holm05], more stable state-of-the-art blue PHOLEDs offer usually greenish blue (sky-blue) emission (see Table 3-1c in chapter 3.1). Consequently, the introduction of present phosphorescent OLEDs into the down-conversion approach only allows the development of warm white-emitting devices due to the high fraction of green light emitted by such PHOLEDs.

using a single imaginary phosphor. The phosphor absorption and re-emission spectra are created by shifting YAG:Ce³⁺ absorption and re-emission spectra 40 nm to longer wavelengths. The sky-blue PHOLED spectrum in Fig. 5-32 corresponds to the emission of the PHOLED presented in chapter 3.2. Using the down-conversion model by Duggal *et al.*, a resulting warm white spectrum complying with color coordinates on the Planckian locus (CIE x/y = 0.38/0.37) has been derived. At present, there is no phosphor material commercially available, which meets these requirements [Jerm06].

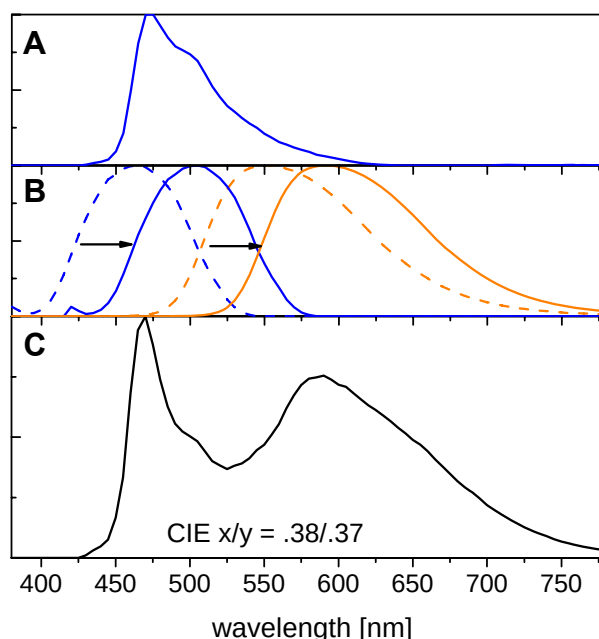


Fig. 5-32. Down-conversion of sky-blue PHOLED emission (A) by an imaginary phosphor. The phosphor absorption and re-emission spectra are created by shifting YAG:Ce³⁺ absorption and re-emission spectra 40 nm to longer wavelengths (B). The calculated warm white spectrum (C) corresponds to CIE color coordinates $x/y = 0.38/0.37$.

However, the incorporation of organic dyes into the down-conversion system might be an approach to obtain lighting devices based on sky-blue PHOLEDs. Fig. 5-33 demonstrates the generation of white light by a multi down-conversion layer system, which comprises a BASF Lumogen F perylene orange (quantum yield > 90 %, [BASF97]) layer, a BASF Lumogen F perylene red (quantum yield > 90 %, [BASF97]) layer and a YAG:Ce³⁺ layer (down-conversion layer system according to [Dugg02]). The spectrum of the underlying sky-blue PHOLED corresponds to the emission of the PHOLED presented in chapter 3.2.

According to the model proposed by Duggal *et al.*, this multi layer system is capable of down-converting sky-blue emission to illumination quality warm white light (CIE $x/y = 0.40 / 0.39$).

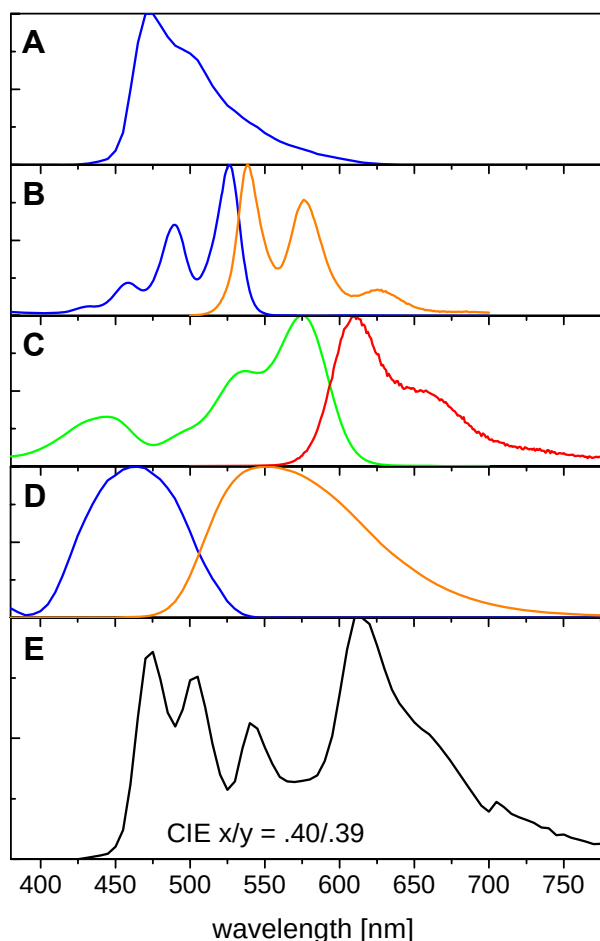


Fig. 5-33. Down-conversion of sky-blue PHOLED emission (A) by a multi down-conversion layer system. The phosphor absorption and re-emission spectra of BASF Lumogen F perylene orange (B), BASF Lumogen F perylene red (C) and YAG:Ce³⁺ (D) are depicted in the figure. The calculated warm white spectrum (E) corresponds to CIE color coordinates $x/y = 0.40/0.39$. The data of the perylene dyes has been obtained from BASF [BASF97].

Conversion factors of $c = 0.87$ for the white based on the imaginary phosphor and $c = 0.79$ for the white based on the multi layer system can be derived, considering the ratio of blue to expected white photometric efficiency. This translates into an expected luminous efficiency of ≈ 17 cd/A and an expected power efficiency of ≈ 11 lm/W, when using the blue PHOLED presented within this work as underlying light source (calculations without changes in light extraction). Comparing these numbers to the expected efficiencies of white devices based on blue emitting fluorescent devices, the advantage of electrophosphorescent devices as

light sources for down-conversion devices becomes obvious. In the field of organic electrophosphorescence significant progress can be expected: Recently, a sky-blue emitting small molecule PHOLED offering 37 lm/W power efficiency has been announced by Kido Laboratories [Kido05].

Furthermore, down-conversion OLEDs will not be restricted to illumination applications; they also offer the potential to realize area color devices for signage applications, for example “EXIT” signs, plates showing a house number or directing arrows. Here area color is given by lateral structured phosphor coatings comprising of luminescence converting materials emitting in different spectral ranges. This approach is much more efficient than creating area color based on a broad band emitting OLED, where the different colors are realized by lateral structured color filters.

Further improvement of OLED lifetime and development of suitable phosphor materials will open up the realization of the down-conversion concept in OLED lighting technology and increase its potential for future lighting applications.

5.4. Conclusion

In conclusion, bottom emitting down-conversion OLEDs have been studied from an optical point of view. Therefore, the optical processes occurring in such devices were translated into a ray-tracing simulation. The methods to obtain all relevant model inputs have been demonstrated by a blue PLED panel and a series of down-conversion layers comprising YAG:Ce³⁺ phosphor and silicone as matrix material. The simulation model has been confirmed experimentally by comparing its predictions derived from ray-tracing simulation to measurements.

In agreement with previous work [Dugg02], both experimental and simulation results have shown that the application of a phosphor layer on the substrate surface of an OLED can lead to an increase in photon extraction efficiency. Considering the influence of phosphor concentration in the matrix and the influence of physical layer thickness on external device efficiency, a maximum in extraction efficiency occurs at a certain value of normalized layer thickness. At lower values, wave-guiding within the substrate is not efficiently suppressed by scattering at the phosphor particles, while, at higher values, more and more light is back-scattered into the OLED stack leading to absorption losses. The maximum value in extraction efficiency is given by the balance of these two effects.

However, the normalized thickness of the down-conversion layers is usually given by the target color coordinates of the resulting device. In the optimum configuration, the fraction of photons, which is necessary to reach the target color coordinates, is converted by the layer and scattering at the phosphor particles leads to efficient light extraction enhancement at the same time. This balance is given by the ratio between scattering and absorption at the phosphor particles. According to MIE-theory the ratio between scattering and absorption probability depends on the phosphor particle size. Using the ray-tracing simulation, the light extraction enhancement due to the phosphor layer has been studied for a set of different phosphor particle size distributions. The obtained results implicate a careful choice of the phosphor powder, since the particle size distribution has a significant impact on the resulting external device efficiency of white light-emitting down-conversion OLEDs. However, it seems hardly possible to develop general design guide-lines for the optimum phosphor particle size distribution, since in each case the target color coordinates and the optical constants of the phosphor material and its matrix have to be considered. But knowing the material properties of the phosphor powder predictions of color coordinates, of extraction efficiencies and of phosphor concentration as well as of physical layer thickness are possible

Additionally, the influence of effective stack reflectance on photon extraction efficiency has been studied. To optimize external device efficiency, an underlying blue OLED offering a high effective stack reflectance should be chosen. In the region of effective reflectance of typical bottom emitting OLEDs a change in reflectance of a few percent has a significant impact on external device efficiency.

Furthermore, the dependence of emission color on the viewing angle has been studied. Experimental results and model predictions showed that the emission color of a flat panel device coated with a phosphor layer is dependent on the viewing-angle. The angular distribution of emission (which is related to the in-coupling angle into the down-conversion layer) and the dependence of phosphor absorption probability on the in-coupling angle lead to a more bluish emission at smaller viewing angles. To overcome this limitation, an innovative approach to reduce the dependence of emission color on viewing angle for down-conversion OLED has been proposed. The feasibility of the approach has been demonstrated by experiment. Using optical half-micro cavity effects the angular distribution of emission within the substrate of blue sm-OLEDs has been modified. The enhancement of blue emission at higher angles acted against the increasing probability of a photon being absorbed by the conversion layer at higher emission angles. This way, the dependence of emission color on viewing angle was reduced without affecting external device efficiency.

Finally, the realization of the down-conversion concept in OLED lighting technology has been discussed. The accomplishment of down-conversion OLEDs will rely on the development of highly efficient blue PHOLEDs. Furthermore, suitable luminescence converting materials have to be developed, which offer the appropriate absorption and re-emission spectra needed to obtain illumination quality white light.

6. Summary and Conclusion

Focus of the present thesis is the generation of white light based on down-conversion of blue OLED emission. The motivation of this work becomes obvious when comparing the down-conversion concept to other approaches, where two or more emissive components provide white light: Down-conversion devices offer better color stability as the aging rate is determined by only one emitter. The approach leads to a less complex architecture of the light source and, thus, can be implemented by easier fabrication techniques due to the presence of one single emitting component. Furthermore, the emission color can be controlled by adjusting the down-conversion layer without affecting the electrical properties of the underlying light source.

However, the resulting efficiency of a down-conversion device is determined by the efficiency of the underlying blue light source. In OLED technology, blue continues to be the most difficult portion of the spectrum for which to find efficient systems. A simple experimental approach in order to harvest triplets and singlets in blue-emitting organic electrophosphorescent devices has been demonstrated in this work. The use of an uncomplicated, bilayer device architecture has enabled the fabrication of electrophosphorescent OLEDs based on solution processing with performance rivaling those of published multilayer small molecule electrophosphorescent OLEDs. The evolution of device efficiency for this class of OLEDs with different hole-electron balance in the light-emitting polymer layer was studied. While charge balance was observed to play a major role, optical half-micro cavity effects also contribute to the improved efficiency. These effects are determined by the location of the exciton profile within the light-emitting layer, and are often not taken into consideration when analyzing the effect of charge balance on device performance. By simulation based analysis, the changes in electroluminescence spectra from a series of devices the location of the emission zone within the light-emitting polymer layer could be pinpointed, from which the half-cavity effects were quantified. Based on this, for the first time a general methodology has been demonstrated, which allows determining the contribution of both charge balance and optical effects while analyzing the performance of devices.

An advantageous side effect of a down-conversion layer applied on the substrate surface of a blue OLED can be light extraction enhancement due to scattering by phosphor particles. In general, modifying the light emitting surface is a well-known approach to increase the external light output of OLEDs. This approach relies on the extraction of light which would be wave-guided within the substrate of the unmodified device. Thereby the apparent light extraction enhancement is given by the ratio between the efficiency of the unmodified device and the efficiency of the modified device. As one of the results of this work, it has been demonstrated that the apparent effectiveness of light outcoupling enhancement by using a method of modifying the substrate surface is significantly dependent on the device structure itself. Hence, this apparent effectiveness is not the correct value to judge the effectiveness of a technique to enhance light outcoupling due to substrate surface modification. In this thesis, a general method to evaluate substrate surface modification techniques for light extraction enhancement of OLEDs has been proposed, which is independent from the device architecture. The ratio between the light output of the surface modified device and the total amount of light which is generated in the device stack and coupled into the substrate, is a more accurate parameter to describe the light extraction enhancement properties. In the optimal case, the ratio would be 1, which corresponds to a light outcoupling methodology completely suppressing substrate wave-guiding. Determination of the enhancement properties using the proposed method not only allows the comparison of different methods of substrate surface modifying techniques, but also provides an analytical understanding to enable further improvement of each technique. The method was experimentally demonstrated using green electrophosphorescent OLEDs with different device architectures. The substrate surface of these OLEDs was modified by applying a prismatic film to increase light outcoupling into the ambient.

In contrast to the common misunderstanding that light outcoupling efficiency is about 22 % and independent from device architecture, the device data and optical modelling results clearly demonstrated that the light outcoupling efficiency is strongly dependent on the exact location of the recombination zone. Estimating the device internal quantum efficiencies based on external quantum efficiencies without considering the device architecture, could lead to erroneous conclusions.

Further, a wavelength dependence of the apparent effectiveness of light outcoupling enhancement due to substrate surface modification has been shown. This is another reason why the apparent effectiveness is not the correct value to judge the effectiveness of a substrate surface modification. The dependence of the apparent light outcoupling enhancement leads to

changes in the output spectrum, when modifying the substrate surface of an organic EL-device emitting in a broad range of wavelengths. Thus, when adjusting the spectral emission of a white light-emitting OLED, the optical interaction between OLED and substrate surface modification has to be considered within the process of device development.

Finally, down-conversion OLEDs have been studied from an optical point of view. Therefore the optical processes occurring in such devices were translated into a ray-tracing simulation. The methods to obtain all relevant model inputs have been demonstrated by a blue polymer OLED panel and a series of down-conversion layers comprising of YAG:Ce³⁺ particles (yttrium aluminum garnet doped with cer) as phosphor. The simulation model has been confirmed experimentally by comparing its predictions derived from ray-tracing simulation to measurements. In agreement with previous work in the field, both experimental and simulation results have shown that the application of a phosphor layer on the substrate surface of an OLED can lead to an increase in photon extraction efficiency. Considering the influence of phosphor concentration in the matrix and the influence of physical layer thickness on external device efficiency, a maximum in extraction efficiency occurs at a certain value of normalized layer thickness (the normalized layer thickness has been defined as the product of volumetric phosphor concentration and physical layer thickness). At lower values of normalized layer thickness, wave-guiding within the substrate is not efficiently suppressed by scattering at the phosphor particles, while at higher values, more and more light is back-scattered into the OLED stack leading to absorption losses. The maximum value in extraction efficiency is given by the balance of these two effects.

However, the normalized thickness of the down-conversion layers is usually given by the target color coordinates of the resulting device. In the optimum configuration, the fraction of photons, which is necessary to reach the target color coordinates, is converted by the layer and scattering by the phosphor particles leads to efficient light extraction enhancement at the same time. This balance is given by the ratio between scattering and absorption at the phosphor particles. According to MIE-theory, the ratio between scattering and absorption probability depends on the phosphor particle size distribution. Using the ray-tracing simulation, the light extraction enhancement due to the phosphor layer has been studied for a set of different phosphor particle size distributions. The obtained results implicate a careful choice of the phosphor powder, since the particle size distribution has a significant impact on the resulting external device efficiency of white light-emitting down-conversion OLEDs. However, it seems hardly possible to develop general design guide-lines for the optimum phosphor particle size distribution, since in each case the target color coordinates and the

optical constants of the phosphor material and its matrix have to be considered. But case studies for certain known phosphors are possible and will enable the build-up of efficient OLEDs offering the right spectral emission characteristics. The simulation model can also be transferred to the inorganic chip level conversion LEDs.

Additionally, the role of effective stack reflectance of the underlying blue OLED has been studied as a further influence on photon extraction efficiency of down-conversion OLEDs. To achieve optimum external device efficiency, the blue OLED should offer high effective stack reflectance. Ray-tracing simulation results show, that in the region of effective stack reflectance of typical bottom emitting OLEDs, a change in reflectance of a few percent has a significant impact on external device efficiency.

Furthermore, the emission color as a function of viewing angle has been studied. Experimental results and model predictions show that the emission color of a flat panel device coated with a phosphor layer is dependent on the viewing-angle. The angular distribution of light coupled into the down-conversion layer and the dependence of the average phosphor absorption probability on the in-coupling angle lead to a more bluish emission at smaller viewing angles. An innovative approach to reduce the dependence of emission color on viewing angle for down-conversion OLED has been proposed to overcome this limitation. The feasibility of the approach has been demonstrated by experiment. By using half-cavity effects, the angular distribution of emission within the substrate of blue small molecule OLEDs has been adjusted. Thereby, the emission intensity has been enhanced at higher angles with respect to the substrate normal. This procedure is contrary to the usual device optimization, where the emission is directed into a preferably small range of solid angle in order to minimize losses due to total internal reflection at the interface between glass and air. The enhancement of emission at higher angles acts against the increasing probability of a photon being absorbed by the conversion layer at higher emission angles. The dependence of emission color on viewing angle was reduced this way. At the same time, the external device efficiency was not affected, when comparing the obtained efficiency to a down-conversion device with an OLED of typical optimization as underlying light source. This can be explained by light scattering by phosphor particles, which leads to the extraction of wave-guided light.

Finally, the realization of the down-conversion concept in OLED lighting technology has been discussed. The accomplishment of down-conversion OLEDs will rely on the development of highly efficient blue electrophosphorescent OLEDs and improvement of their stability. Furthermore, suitable luminescence converting materials have to be developed,

which offer the appropriate absorption and re-emission spectra needed to obtain illumination quality white light. Down-conversion OLEDs will not be restricted to illumination applications; they also offer the potential to realize area color devices for signage applications. The down-conversion approach is much more efficient than creating area color based on a broad band emitting OLED, where the different colors are realized by lateral structured color filters.

Appendix

A The Kubelka-Munk Function

The Kubelka-Munk function [Kube31] is a useful equation for the optical characterization of phosphor powders from a phenomenological point of view. The equation links the reflectance of an absorbing and scattering powder layer of infinite thickness to its scatterance S and to the absorption coefficient K in the case of non-directional light incidence. In the following, the function is derived from 4-channel theory [Völz01]. This theory is based on a model shown in Fig. A-1. The intensities of four rays are considered (represented by arrows), which propagate through an absorbing and scattering layer of thickness t . In particular, these ray-intensities are given by:

- directional incidence of light: I^+
- directional light in the opposite direction: I^-
- diffuse incidence of light: L^+
- diffuse light in the opposite direction: L^-

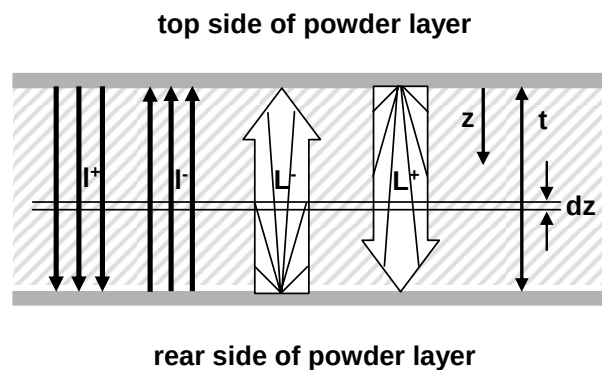


Fig. A-1. 4-channel theory: directional ray intensities I^+ , I^- and diffuse ray intensities L^+ , L^- propagating in a powder layer of thickness t (adapted from [Völz01]).

In Fig. A-1, z is a coordinate in the direction of light incidence. It is now considered how the ray intensities are changed when propagating a small distance dz . Analogous to the rule of Lambert-Beer, I^+ decreases by $-k' I^+ dz$ due to absorption. Here k' is defined as the absorption coefficient of directional light. Furthermore, I^+ decreases by the fraction of light which is scattered in front direction $-s^+ I^+ dz$, and by the fraction of light $-s^- I^+ dz$, which is back-scattered. Thereby s^+ and s^- are defined as the scatterance of directional light for front and back-scattering, respectively. Thus, the change in ray intensity of directional light incidence is given by:

$$(Eq. A-1) \quad dI^+ = -(k' + s^+ - s^-) I^+ dz .$$

Accordingly, the change in ray intensity of directional light in the opposite direction is given by:

$$(Eq. A-2) \quad -dI^- = -(k' + s^+ - s^-) I^- dz .$$

The ray intensity of diffuse light L^+ is considered next. Analogous to I^+ , L^+ is reduced by the absorbed fraction $-K L^+ dz$ and by the scattered fraction $-S L^+ dz$ (K is the absorption coefficient and S the scatterance for diffuse light). Furthermore, L^+ increases by the scattered fraction of I^+ and I^- , respectively ($s^+ I^+ dz$ and $s^- I^- dz$). The scattered fraction of diffuse light propagating into the opposite direction has to be added (SL^-). The change in L^+ and L^- is given by:

$$(Eq. A-3) \quad dL^+ = s^+ I^+ dz + s^- I^- dz - (K + S) L^+ dz + S L^- dz \quad \text{and}$$

$$(Eq. A-4) \quad -dL^- = s^- I^+ dz + s^+ I^- dz - (K + S) L^- dz + S L^+ dz .$$

Eq. A-5 and Eq. A-6 summarize all coefficients and their definitions:

$$(Eq. A-5) \quad k' = \left. \frac{1}{I} \frac{dI}{dz} \right|_{abs}, \quad s^+ = \left. \frac{1}{I} \frac{dI}{dz} \right|_{front s}, \quad s^- = \left. \frac{1}{I} \frac{dI}{dz} \right|_{back s},$$

$$(Eq. A-6) \quad K = \frac{1}{L} \frac{dL}{dz} \Big|_{abs}, \quad S = \frac{1}{L} \frac{dL}{dz} \Big|_s.$$

Considering the case of non-directional light incidence, I^+ and I^- are set equal to zero. Thus, Eq. A-3 and Eq. A-4 are reduced to:

$$(Eq. A-7) \quad dL^+ = -(K + S)L^+ dz + SL^- dz,$$

$$(Eq. A-8) \quad -dL^- = -(K + S)L^- dz + SL^+ dz.$$

Furthermore, Eq. A-7 is divided by SL^+ and Eq. A-8 is divided by SL^- :

$$(Eq. A-9) \quad \frac{1}{S} \frac{1}{L^+} \frac{dL^+}{dz} = -\left(1 + \frac{K}{S}\right) + \frac{L^-}{L^+},$$

$$(Eq. A-10) \quad \frac{1}{S} \frac{1}{L^-} \frac{dL^-}{dz} = -\left(1 + \frac{K}{S}\right) - \frac{L^+}{L^-}.$$

A powder layer of thickness t has the same reflectance as a layer of infinite thickness, if a further increase in layer thickness would lead to no change in reflectance. In this case, the change in ray intensity in front direction ($1/L^+ \cdot dL^+/dz$) would be equal to the change in ray intensity in the opposite direction ($1/L^- \cdot dL^-/dz$). Finally, by setting Eq. A-9 equal to Eq. A-10, the Kubelka-Munk function is derived:

$$(Eq. A-11) \quad \frac{K}{S} = \frac{(1 - R_\infty)^2}{2 R_\infty}, \quad R_\infty = \frac{L^-}{L^+},$$

where R_∞ is the reflectance of a powder layer of infinite thickness.

B Annotations to Chapter 3

PL-Spectra and Quantum Efficiency of FIrpic in PVK

The presence of OXD-7 in the PVK matrix can be expected to have an effect on two parameters: the PL-spectrum of the film itself and the intrinsic quantum efficiency of the film. Only, if both parameters are not affected by the presence of OXD-7, conclusions about EL spectral and efficiency changes are valid. Both effects are excluded as follows:

Changes in PL spectra - An influence on the PL-spectrum of FIrpic with increased OXD-7 concentration may be expected to take place based on the solid state salivation effect as reported by Bulovic *et al.* [Bulo99]. Normalized PL-spectra of the devices with 0 %, 20 % and 40 % OXD-7 are shown in Fig. B-1a. There are no changes in the PL-spectra due to the different OXD-7 concentrations observed.

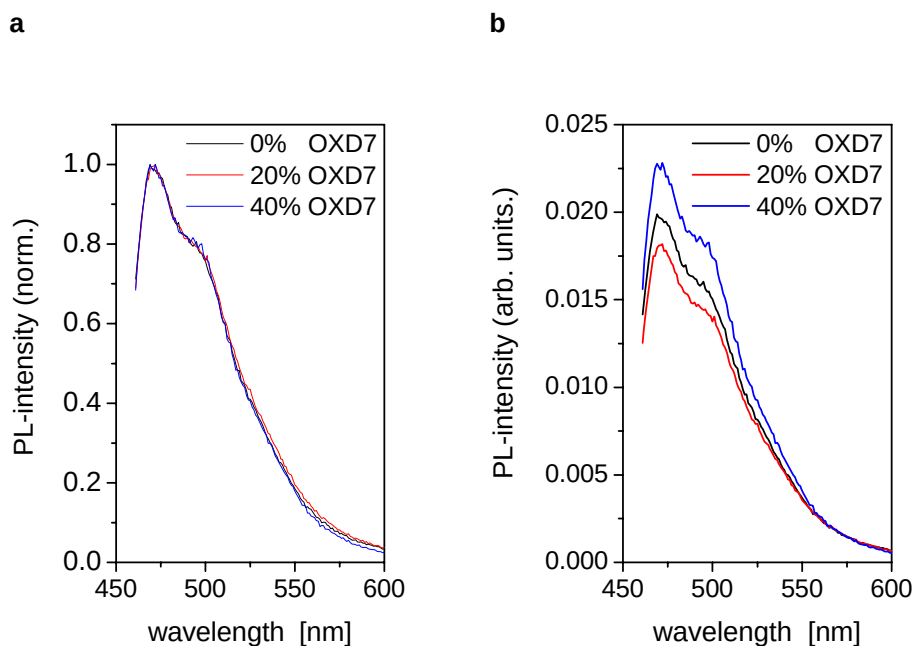


Fig. B-1. PL-spectra of the devices with 0 %, 20 % and 40 % OXD-7. (a) normalized data, (b) raw data. Measurements were performed using a Shimadzu RF-5301 PC spectrofluorophotometer (excitation wavelength 450 nm).

Quantum efficiency of the films - It has to be noted that in the case of phosphorescence based PL efficiency, while there is a strong dependence of PL quantum efficiency on the dye concentration (for example [Kawa05]), this cannot be said for another component added to the film which is not the actual phosphorescent emitter. Besides, performing a similar experiment was impossible as at the point of time of the experiments there was a lack of availability of a setup where all the light from a substrate in a photoluminescence measurement could be collected. At the same time, the results plotted in Fig. B-1 indicate that there is no trend of PL intensity observed with increasing concentrations of OXD-7 in the film. Prior results have also clearly shown that the main factor determining the quantum efficiency of the emissive layer in an OLED format is governed more by the phenomena of direct injection into the dye molecule [Chou05]. As such, it is difficult to correlate PL quantum efficiency with EL quantum efficiency directly.

Error Estimation due to Limited Accuracy of Analysis

In the following, the accuracy in the separate quantification of efficiency improvement due to charge balance and the improvement due to the change in the location of the EMZ is discussed. The calculation of this quantitative separation was based on a full width at half maximum (FWHM_{EMZ}) of 20 nm for the imaginary devices A', B', C', D', E'. Varying the values of the FWHM_{EMZ} in the range between 5 nm and 40 nm, the corresponding EL-spectra in the direction of the substrate normal for the devices A', B', C', D', E' were obtained by simulation. When changing the FWHM_{EMZ} , no significant difference in the shape of the EL-spectrum was observed for each device. Thus, the measured EL-spectra of the real devices A, B, C, D, E can be fitted assuming values of the FWHM_{EMZ} in the range between 5 nm and 40 nm. Furthermore, the external light output of the imaginary devices A', B', C', D', E' was simulated as a function of the FWHM_{EMZ} . For devices B' and C', the output was calculated in the range from 5 nm to 40 nm. For the device A', D', E' the range was limited to values smaller than 40 nm, since the location of the EMZ is closer to the border of the LEP. In the plot of Fig. B-2, the normalized computed light output of the devices B', C', D', E' is depicted as a function of wavelength. For each device, a minimum and a maximum light output ($O_{\min}(X')$ and $O_{\max}(X')$, ($X' \in [B', C', D', E']$)) is given. The error-bars in the plot of the improvement due to better charge balance in comparison to device A (Fig. 3-8) are calculated, based on $O_{\min}(X')$ and $O_{\max}(X')$ according to Eq. 3-2. A comparison of the magnitude of the

error to the measured light output (Fig. 3-8) is a measure of the accuracy in the quantitative separation of the two effects.

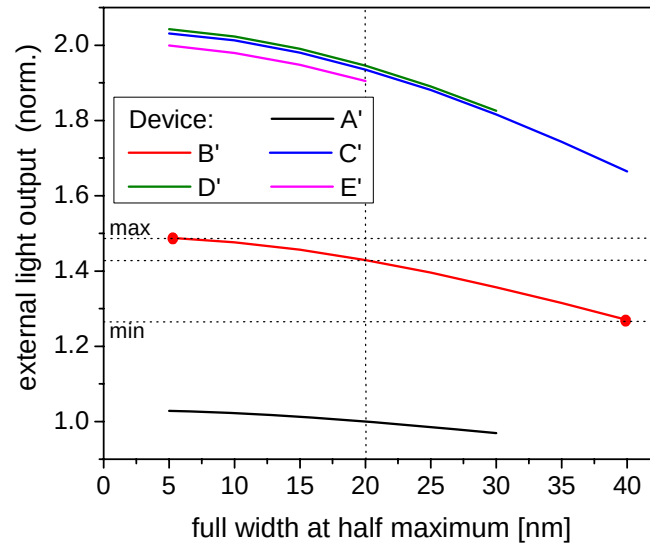


Fig. B-2. Simulation of the external light output as a function of the $FWHM_{EMZ}$ for the imaginary devices A', B', C', D', E'. For device B', the minimum and maximum light output (i.e. the minimum and maximum improvement due to optical half-micro cavity effects in comparison to device A') is marked, which was obtained by varying the $FWHM_{EMZ}$ in the range between 5 nm and 40 nm.

C Annotations to Chapter 4

In the following it is demonstrated, that the extraction efficiency η_{s-a} (definition see chapter 4.2) is nearly independent from the angular distribution of emission when using a certain substrate surface modification for light extraction enhancement. Light extraction enhancement due to the prismatic film (BEF) used for the study, presented in chapter 4, and light extraction enhancement due to a diffusive layer described by Nakamura in reference [NakaT04] has been analysed using ray-tracing simulation. The ray-tracing model proposed in chapter 5 has been modified for this purpose. In the model the conversion layer has been replaced by either the BEF structure (see chapter 4) or by a diffusive layer. The angular distributions of emission within the substrate used for this analysis have been derived from the optical simulations of the green emitting devices with the different Alq_3 layer thicknesses, which are presented in chapter 4 (see Fig. C-1). The effective reflectance of the OLED was set independent from wavelength at a fixed value of $R_{\text{OLED}} = 0.8$, which corresponds to a typical bottom emitting OLED [Shiang04a].

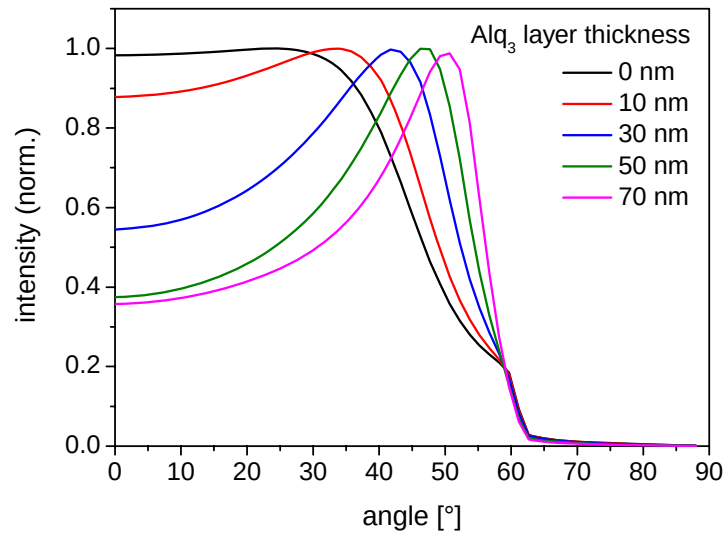


Fig. C-1. The angular distributions of emission within the substrate derived from the optical simulations of the green emitting devices with the different Alq_3 layer thicknesses, which are presented in chapter 4.

Brightness Enhancement Film

Table C-1 summarizes the extraction efficiencies η_{s-a} obtained by the ray-tracing simulation of the devices with the BEF. Here η_{s-a} corresponds to the ratio $I_{film}:I_{gel}$ determined by measurement for each value of Alq₃ layer thickness (see chapter 4). The simulated values are nearly independent from the angular distribution of emission within the substrate. According to the simulation, the extraction efficiency of the devices with the BEF is approximately 0.58, which is close to the value of the ratio $I_{film}:I_{gel} \approx 0.6$ determined by measurement (see Table 4-3).

Table C-1. Values of extraction efficiency η_{s-a} obtained by simulation of the devices equipped with the BEF.

Alq ₃ layer thickness	η_{s-a}
0	0.59
10	0.59
30	0.59
50	0.57
70	0.55

Diffusive Layer

The diffusive layer was modelled according to data which is given in work published by Nakamura [NakaT04]. Here the scattering layer consisted of PMMA (refractive index $n \approx 1.5$) containing 5 % by weight rutile titanium dioxide particles (average diameter 0.5 μm). Scattering in the diffusive layer was simulated analogously to the simulation of the down-conversion layers reported in chapter 5. Absorption by titanium dioxide was neglected, i.e. the absorption probability in the simulation was set equal to 0. The simulated values of extraction efficiency η_{s-a} for the devices equipped with the diffusive layer are given in Table C-2. In the case of the diffuse layer, the extraction efficiency is $\eta_{s-a} \approx 0.58$ and shows hardly any dependence from the angular distribution of emission within the substrate.

Table C-2. Values of extraction efficiency η_{s-a} obtained by simulation of devices equipped with a diffusive layer.

Alq ₃ layer thickness	η_{s-a}
0	0.58
10	0.58
30	0.58
50	0.57
70	0.56

D The Henyey-Greenstein Scattering Function

According to MIE-theory, the mathematical expression of the scattering function is quite complex (see chapter 2.5.B). The Henyey-Greenstein (HG) scattering function [Heny41] is widely used to model scattering at particles of broad size distribution. The one parameter form of this empirical description of the scattering function is given by:

$$(Eq. D-1) \quad p(\cos \vartheta) = \frac{1}{2} \frac{1 - g^2}{(1 + g^2 - 2g \cos \vartheta)^{3/2}},$$

where g , the assymetry factor, is the expectation value of $\cos(\vartheta)$ and ϑ is the scattering angle defined as the angular difference between the original and the new propagation direction of the photon after a scattering event. Thus, $g = 1$ implies that each scattering event does not deflect the beam, $g = -1$ implies that each scattering event back-scatters the beam along the incident direction, and $g = 0$ implies isotropic scattering. Fig. D-1 shows scattering functions due to Henyey and Greenstein for various values of g in the range between 0 and 0.9.

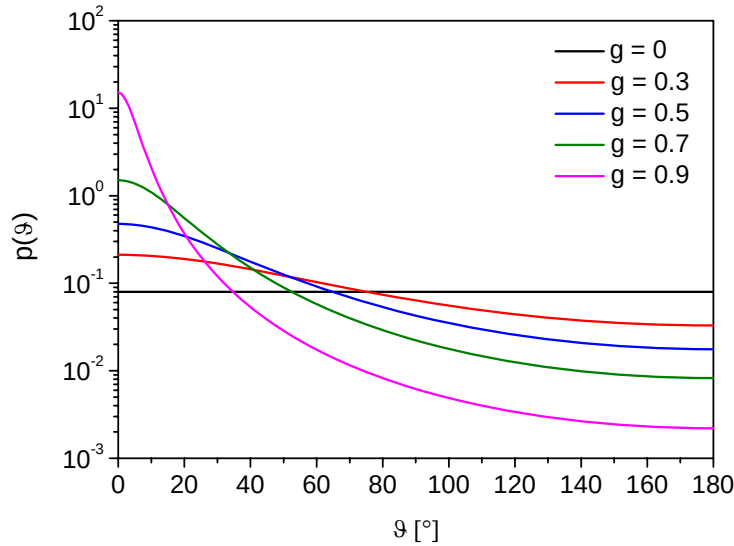


Fig. D-1. Logarithmic plot of scattering functions due to Henyey and Greenstein for g -factors in the range between 0 and 0.9.

E Logarithmic Plot of Scattering Functions

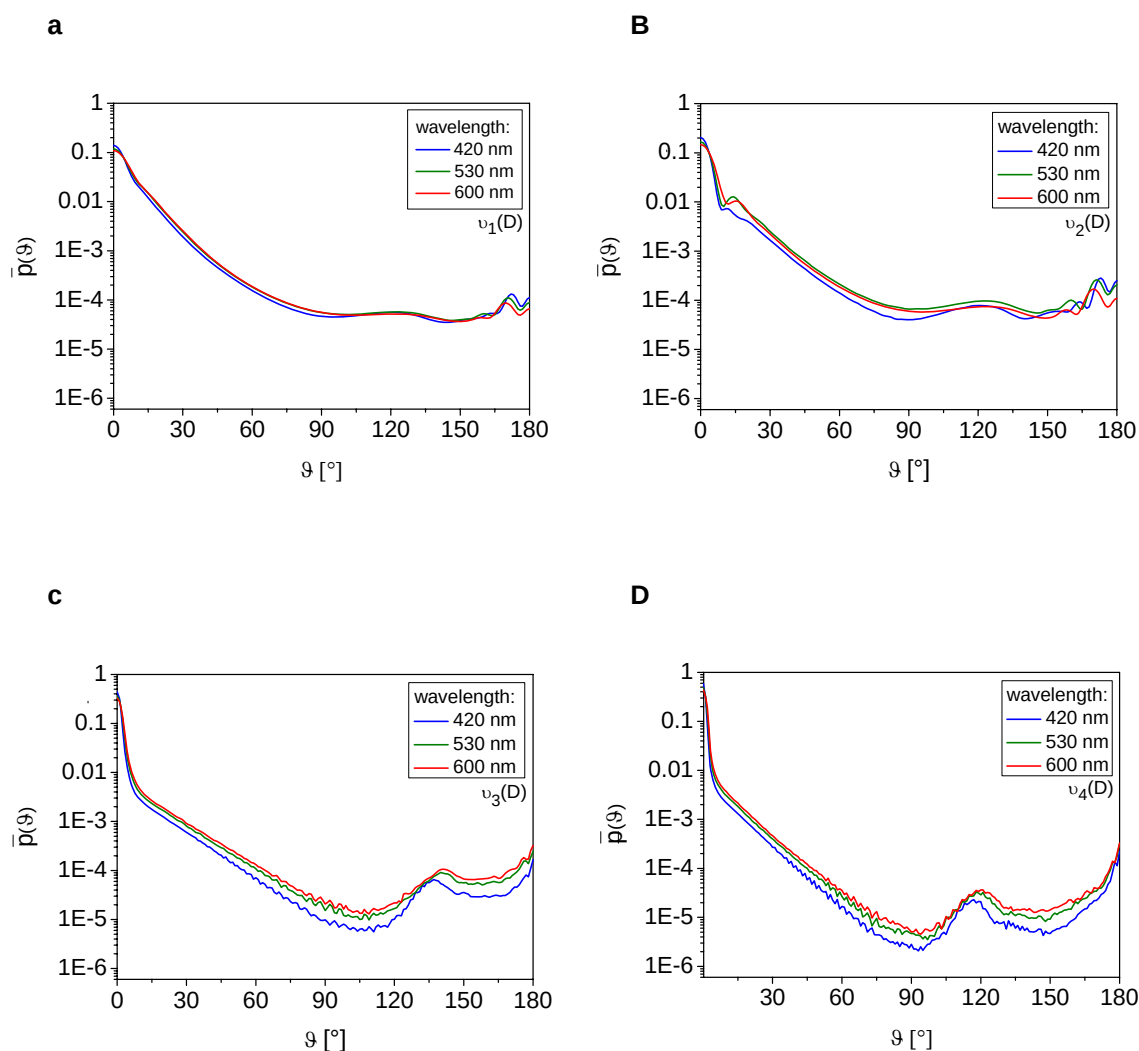


Fig. E-1. Logarithmic plots of the average scattering functions in silicone corresponding to the YAG:Ce³⁺ phosphor particle size distributions $\nu_1(D)$, $\nu_2(D)$, $\nu_3(D)$, $\nu_4(D)$.

F Optical Data of Materials used within this Work

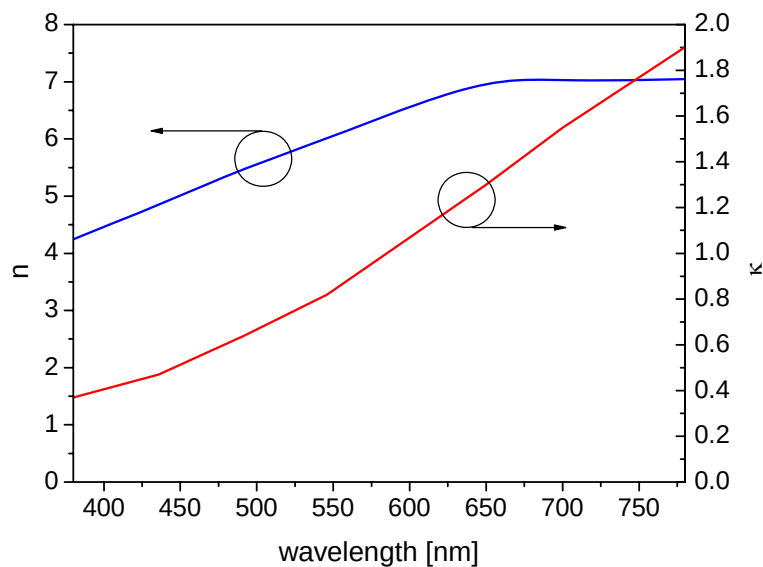


Fig. F-1. Aluminum - complex refractive index as a function of wavelength [Buch05].

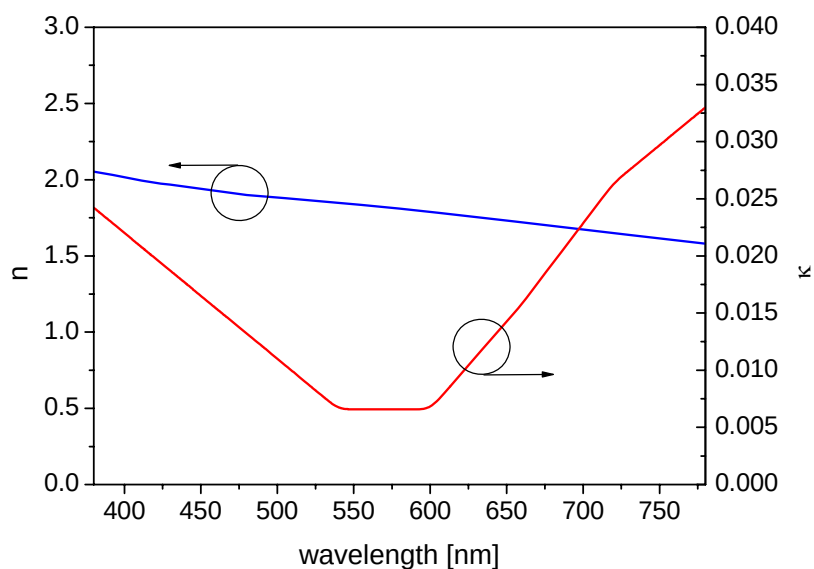


Fig. F-2. ITO - complex refractive index as a function of wavelength [Buch05].

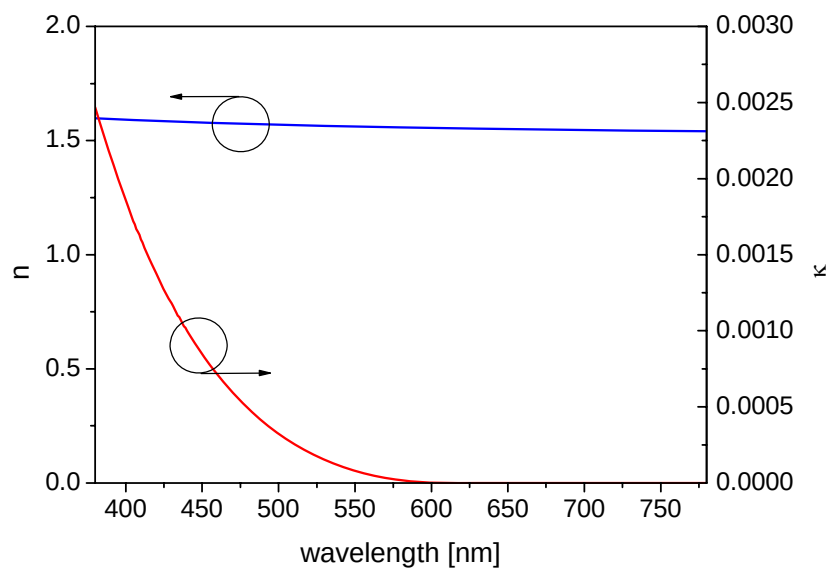


Fig. F-3. PEDOT:PSS - refractive index as a function of wavelength [Buch05].

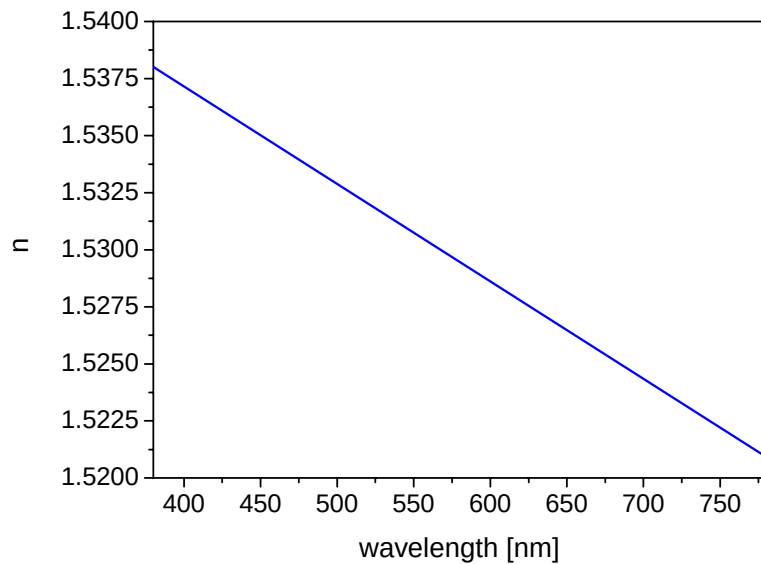


Fig. F-4. Silicone used as matrix of the down-conversion layers - refractive index as a function of wavelength.

G Abbreviations

Chemical Compounds

2-TNATA	4,4',4''-tris(N-(2-naphtyl)-N-phenylamino)triphenylamine
4P-TPD	4,4'-bis-(N,N-diphenylamino)-tetraphenyl
Al	Aluminum
Alq ₃	tris(8-hydroxyquinoline) aluminum
Ba	Barium
BAlq	4-biphenyloxolato-aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate
BCP	Bathocuproine
BCzVB	1,4-bis[2-(3-N-ethylcarbazoryl)vinyl]benzene
BD1	a mono(styryl)amine-based blue dopant [Lee05]
BDPQ	6,6'-bis(2,4-diphenylquinoline)
BDPVPA	9,10-bis-[4-(2,2-diphenylvinyl)-phenyl]-anthracene
BPhen	4,7-diphenyl-1,10-phenanthroline
Ca	Calcium
CBP	4,4'-dicarbazolyl-1,1'-biphenyl
CFx	polymerized fluorocarbon
c-HTL	CuPc/NPB composite HTL
CsF	caesium fluoride
CuPc	copper phthalocyanine
DAS-Ph	p-bis(p-N,N-diphenyl-aminostyryl)benzene-doped
DNA	9,10-bis-(β -naphthyl)-anthrene
DPF	2,7-dipyrene-9,9'-dimethylfluorine

DPVBi	4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl
F4-TCNQ	2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane
FIr6	iridium(III) bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate
FIrpic	iridium(III)bis[(4,6-di-fluorophenyl)-pyridinato-N,C ²]picolinate
Ir(ppy) ₃	fac-tris(2-phenylpyridine)iridium
ITO	indium tin oxide
LiOXD	2-(5-phenyl-1,3,4-oxadiazolyl)-phenolatolithium
LiPBO	2-(2-hydroxyphenylbenzoxazole)
MADN	2-methyl-9,10-di(2-naphtyl)-anthracene
mCP	N,N'-dicarbazolyl-3,5-benzene
MeO-TPD	N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine
m-Ir(pmb) ₃	tris(phenyl-methyl-benzimidazolyl)iridium(III)
MPS	1-methyl-1,2,3,4,5-pentaphenylsilole
MTDATA	4,4',4''-tris{N,-(3-methylphenyl)-N-phenylamino} triphenylamine
NCB	4-(N-carbazolyl)-4'-(N-phenylnaphthylamino)biphenyl
NPB	N,N'-diphenyl-N,N'-bis(1-naphtyl)-(1,1'-biphenyl)-4,4'diamine
OXD-7	1,3,4-oxadiazole,2,2'-(1,3-phenylene)bis(5-(4-(1,1-dimethylethyl)phenyl))
PANI	Polyaniline
PBD	2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole
PEDOT	poly(3,4)-ethylendioxythiophene
PMMA	poly-methyl-methacrylate
PSS	poly(styrene-sulfonate)
PVK	Polyvinylcarbazole
spiro-DPVBi	2,2',7,7'-tetrakis(2,2-diphenylvinyl)spiro-9,9'-bifluorene

spiro-TAD	2,2',7,7'-tetrakis-(n,n-diphenylamino)-9,9'-spirobifluoren
TAZ	3-(4-biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole
TBPSF	2,7-bis[2-(4-tert-butylphenyl)pyrimidine-5-yl]-9,9'-spirobifluorene
TBVB	2,5,2',5'-tetrakis (4'-biphenylenevinyl)-biphenyl
TCTA	4',4''-tris(carbazol-9-yl)-triphenylamine
TPBI	1,3,5-tri(phenyl-2-benzimidazolyl)-benzene
TPD	4,4'-bis(m-tolylphenylamino)biphenyl
TPF	7,8,10-triphenylfluoranthene
TSB	2,5,2',5'-tetrastaryl-biphenyl
UGH2	p-bis(triphenylsilyl)benzene
YAG:Ce ³⁺	yttrium aluminum garnet doped with cer ions

Frequently Used Abbreviations

a	apparent light outcoupling enhancement
BEF	Brightness Enhancement Film
c	conversion factor
CIE	International Commission on Illumination (Comission Internationale de l'Éclairage)
D	particle diameter
$D(\alpha)$	angular distribution of emission within the substrate
d_{norm}	normalized layer thickness
$E(z)$	exciton profile within the emission layer
EL	electroluminescence
$EL_0(\lambda)$	electroluminescence spectrum of the emitter in a space filled with the emitting medium without any interfaces
EML	emission layer
EMZ	emission zone
ETL	electron transport layer
F	flux
g	expectation value of the cosine of the scattering angle ϑ
HOMO	highest occupied molecular orbital
HTL	hole transporting layer
LED	light-emitting diode
LEP	light-emitting polymer layer
LUMO	lowest unoccupied molecular orbital
$MFPW$	mean free path way between two photon impingements at phosphor particles
n	refractive index

N	particle density (number of particles per unit volume)
$n_{phos}^*(\lambda)$	complex refractive index of phosphor material
n_g	refractive index of the substrate glass
n_{matrix}	refractive index of the matrix material of the down-conversion layer
OLED	organic light-emitting diode
$p(D)$	particle size distribution
$p(\vartheta, \lambda)$	scattering function
$P_{abs}(\lambda)$	absorption probability
PHOLED	electrophosphorescent OLED
PL	photoluminescence
PLED	polymer OLED
$Q_A(\lambda)$	absorption cross section
$Q_S(\lambda)$	scattering cross section
QY	quantum yield of luminescence conversion
$R_{OLED}(\lambda)$	effective reflectance of underlying OLED
$S_c(\lambda)$	re-emission spectrum of luminescence converting material
sm-LED	small molecule OLED
$S_{OLED}(\lambda)$	emission spectrum of the underlying blue OLED
z	coordinate in the direction of the substrate normal
Φ	work function
ϑ	scattering angle
α	angle of photon propagation within substrate
$\varepsilon_{phos}^*(\lambda)$	complex dielectric constant of phosphor material
η_{ext}	external quantum efficiency

η_{OLED-s}	fraction of the generated photons that is coupled into the substrate
η_{ph}	total photon extraction efficiency
η_{s-a}	fraction of photons that is coupled into the substrate, which is extracted into the ambient
θ	emission angle

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Einleitung

Motivation

Seit der „Erfindung“ eines brennenden Astes vor 500 000 Jahren ist das Thema Beleuchtung ein wichtiger Aspekt im Alltag des Menschen. Fackeln, später Kerzen und Öllampen, führten zu einer Trennung zwischen den Funktionalitäten „Beleuchten“ und „Heizen“. Gaslampen (1772), elektrische Lampen (1876) und Leuchtstofflampen (1938) stellen Meilensteine der Beleuchtungstechnologie dar.

Betrachtet man den gesamten Primärenergieverbrauch, so werden weltweit 20 Prozent der generierten Elektrizität zu Beleuchtungszwecken verwendet [Misr06]. In dieser Zahl spiegelt sich die Bedeutung von Beleuchtungseinrichtungen im täglichen Leben wieder. In Anbetracht zunehmender Umweltprobleme aufgrund des weltweit wachsenden Energieverbrauchs unterstreicht diese Zahl weiterhin, dass die Entwicklung hocheffizienter Lichtquellen von großer Relevanz ist. Ausgehend von der Erfindung der roten anorganischen Leuchtdiode (LED) im Jahre 1962 [Holo62] hat sich die optische Halbleitertechnologie so weit entwickelt, dass es heutzutage möglich ist, Glühlampen und Leuchtstoffröhren durch effizientere Lichtquellen zu ersetzen. Man schätzt, dass der weltweite Verbrauch elektrischer Energie für Beleuchtung bis zum Jahr 2025 durch die optische Halbleitertechnologie um 50 Prozent reduziert werden könnte [DOE01]. Nun steht eine neue, auf organische Halbleiter beruhende Technologie kurz davor auf den Beleuchtungsmarkt zu drängen.

Ausgangspunkt der Entwicklung von organischen Leuchtdioden (OLEDs) war eine Veröffentlichung von C.W. Tang und S.A. Vanslyke im Jahre 1987 [Tang87]. Diese Arbeit berichtet von der Elektrolumineszenz dünner Schichten, bestehend aus kleinen organischen Molekülen, die durch einen Aufdampfprozess abgeschieden wurden. Drei Jahre später demonstrierten Borroughes et al., dass ein solches Bauteil auch unter Verwendung von Polymeren gefertigt werden kann [Burr90]. Heutzutage beschäftigen sich zahlreiche akademische und industrielle Forschungsgruppen sowohl mit Polymer OLEDs, deren Herstellung auf einen Lösungsmittel basierten Prozess beruht, als auch mit OLEDs, deren organische Schichten durch das Aufdampfen kleiner Moleküle prozessiert werden (engl.

small molecule OLEDs). Im Jahr 1997 wurde als erstes kommerzielles Produkt dieser Technologie ein small molecule OLED Display von Pioneer auf den Markt gebracht. Die erste kommerzielle Anwendung einer Polymer OLED war die Anzeige eines Rasiergerätes von Phillips [Phil03].

Die OLED-Technologie ist mittlerweile soweit ausgereift, dass sie kurz davor steht in den Beleuchtungssektor vorzudringen. Die einzigartigen Vorteile der OLEDs werden zu innovativen Produkten und zu neuartigen Anwendungsfeldern führen: OLEDs sind flach und leicht. Die Dicke der eigentlichen Diode, bestehend aus den organischen Schichten und den sie umgebenden Elektroden, ist geringer als 1 Mikrometer. Die Dicke des gesamten Bauteils wird hauptsächlich durch das Substrat und durch die Verkapselung bestimmt. Der aktuelle Stand der Technik erlaubt Bauteildicken unter 1 Millimeter. Weiterhin bietet die Technologie die Möglichkeit großflächige Lichtquellen in einem billigen und einfachen Prozess zu fertigen.

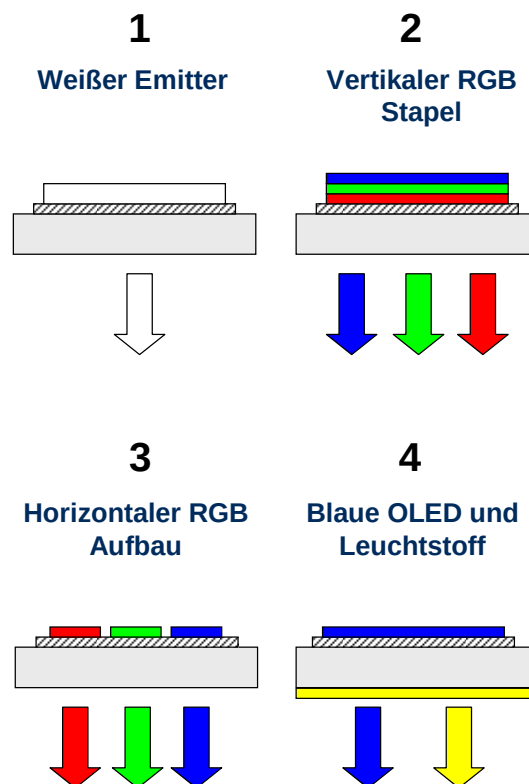


Abb. 1. Schematische Darstellung der 4 verschiedenen Ansätze für den Aufbau weiß emittierender OLEDs.

Abbildung 1 zeigt die vier prinzipiellen Ansätze für den Aufbau weißer OLEDs. Ansatz (1) ist eine OLED, bei der sich mehrere verschiedenfarbig emittierende Komponenten in einer organischen Schicht befinden und somit weißes Licht durch die Superposition der Emission der einzelnen Komponenten entsteht [Slyk00]. Ein solches Bauteil kann mit verhältnismäßig niedrigem Aufwand prozessiert werden. Es ist jedoch schwierig die Emissionsfarbe abzustimmen, ohne Änderungen im Schichtaufbau bzw. der Schichtzusammensetzung vorzunehmen, was möglicherweise zu einer Beeinträchtigung der Leistungsmerkmale (Effizienz, Lebensdauer) des Bauteils führen könnte. Ansatz (2) ist die vertikale Anordnung dreier Schichten, die rot, grün bzw. blau emittieren, wobei eine hohe Farbhomogenität über die Leuchtfläche erreicht wird [Shen01]. Jedoch führt diese Diodenarchitektur zu aufwendigeren Fertigungsprozessen. Bei Ansatz (3) sind rot, grün und blau emittierende Komponenten horizontal angeordnet. Dies ermöglicht es durch getrenntes Steuern dieser Komponenten die Emissionsfarbe im Betrieb abzustimmen. Derzeit bekannte Methoden zur Fertigung eines solchen Bauteils beruhen auf teuren Drucktechniken. Durch die unterschiedlich schnelle Alterung der einzelnen Farbkomponenten stellt die Stabilität der Emissionsfarbe über die Lebenszeit bei allen drei Ansätzen ein Problem dar. Ansatz (4) beruht auf einer blau emittierenden OLED in Kombination mit einem Lumineszenz konvertierenden Material (auch Leuchtstoff oder Phosphor). Eine Leuchtstoff enthaltende Schicht, die auf eine blaue OLED aufgebracht wird, absorbiert einen Teil der von der OLED emittierten Photonen und reemittiert sie bei einer längeren Wellenlänge. Die Überlagerung aus der nicht absorbierten Emission der blauen OLED und der Reemission des Leuchtstoffes ergibt weißes Licht. Dieser Ansatz kann durch einfache Herstellungsverfahren realisiert werden und bietet eine gute Farbstabilität über die Bauteillebenszeit, da die Alterung nur durch eine elektrolumineszente Komponente bestimmt wird. Weiß emittierende Bauteile auf Basis der Lumineszenzkonversion von blauen LEDs wurden erstmals von Schlotter et al. publiziert [Schl97] und werden mittlerweile in zahlreichen Produkten angewendet. Im Jahr 2002 veröffentlichten Duggal et al. als erstes eine OLED, deren weiße Emission mit Hilfe einer blauen OLED und eines mehrlagigen Leuchtstoffsystems erreicht wurde [Dugg02]. Duggal et al. stellten 2005 in einer weiteren Veröffentlichung eine auf diesem Aufbau beruhende Leuchtkachel vor, die bei einer Leuchtdichte von 1000 cd/m² weißes Licht von Beleuchtungsgüte mit einer Effizienz von 15 lm/W emittierte [Dugg05].

Inhalt dieser Arbeit

Fokus dieser Arbeit sind weiß emittierende organische Leuchtdioden auf Basis von Lumineszenzkonversion. Dabei werden zwei Aspekte näher betrachtet: Die zugrunde liegenden blaue OLED und das optische Zusammenspiel von OLED und Konversionsschicht.

Bei Konversions-OLEDs bestimmt die blaue OLED nicht nur die erreichbare Effizienz sondern auch den Preis des gesamten Bauteils. So ist es für die Realisierung solcher Bauteile in Beleuchtungsanwendungen von großer Bedeutung blaue OLEDs in einem einfachen und somit kostengünstigen Prozess herzustellen - vorausgesetzt, dass auf diese Weise nicht die Bauteileffizienz beeinträchtigt wird. In Kapitel 3 dieser Arbeit werden effiziente blaue elektrophosphoreszente Leuchtdioden vorgestellt, die aufgrund ihrer einfachen, aus nur zwei organischen Schichten bestehenden Struktur in einem einfachen, auf Lösungsmitteln beruhenden Prozess hergestellt werden können. Für die emittierende Schicht dieser Dioden werden ein elektrophosphorezenter Emmitter und ein nicht konjugiertes Polymer als Matrix, molekular dotiert mit einem Elektronentransporter, verwendet. Weiterhin werden der Einfluss optischer Effekte und der Einfluss des Ladungsträgergleichgewichts in der emittierenden Schicht auf die Bauteileffizienz quantitativ analysiert.

Ein vorteilhafter Nebeneffekt des Aufbringens einer Konversionsschicht auf einer blauen Leuchtdiode ist die Erhöhung der Lichtauskopplung gegenüber dem unbeschichteten Bauteil. Dieser Effekt beruht auf Lichtstreuung an Leuchtstoffpartikeln. Die Modifikation der Licht emittierenden Seite ist ein bereits bekannter Ansatz die externe Effizienz von OLEDs zu erhöhen [NakaT04], [Shia04a], [Shia04b]. Eine allgemeine Herangehensweise für die Bewertung von Substratoberflächenmodifikationen zur Erhöhung der Lichtauskopplung aus OLEDs wird in Kapitel 4 vorgeschlagen. Die Methode wird anhand grün emittierender elektrophosphoreszenter OLEDs dargelegt, deren Substratoberfläche mit einem prismatischen Film versehen wurde, um die Lichtauskopplung aus diesen Bauteilen zu erhöhen.

Unter Verwendung der in Kapitel 4 vorgeschlagenen Methode schließt in Kapitel 5 eine Analyse der externen Effizienz von Konversions-OLEDs an. Dazu werden die in der Konversionsschicht eintretenden physikalischen Prozesse in einer Raytracing Simulation abgebildet. Die Simulation wird zunächst durch den Vergleich mit experimentellen Ergebnissen einer Überprüfung unterzogen. Anschließend werden anhand der Simulation der Einfluss der Reflektivität der zugrunde liegenden OLED und der Einfluss der Korngrößenverteilung des Leuchtstoffpulvers auf die externe Bauteileffizienz untersucht. Dabei werden sowohl Verbesserungsspielräume als auch Herausforderungen bei der Entwicklung von Konversions-OLEDs aufgezeigt. Abschließend wird ein Ansatz gezeigt, der

es ermöglicht, die Homogenität der Emissionsfarbe von Konversions-OLEDs über den Betrachtungswinkel zu verbessern.

Zusammenfassung

Fokus dieser Arbeit sind weiß emittierende organische Leuchtdioden (OLEDs) auf Basis von Lumineszenzkonversion. Bei diesem Ansatz wird eine Leuchtstoff enthaltende Schicht auf eine blau emittierende OLED aufgebracht. Ein Teil der blauen Elektrolumineszenz wird durch Absorption und Reemission durch den Leuchtstoff in längerwelliges Licht konvertiert. Der nicht absorbierte Anteil der blauen Emission und die Reemission des Leuchtstoffs bilden insgesamt ein breitbandiges, weißes Spektrum. Im Vergleich zu anderen Konzepten, bei denen weißes Licht durch zwei oder mehr elektrolumineszente Komponenten erzeugt wird und somit eine Änderung der Emissionsfarbe durch unterschiedlich schnelle Degradation der Einzelkomponenten auftreten kann, bieten Konversions-OLEDs eine bessere Farbstabilität über die Lebensdauer, da die Alterung nur durch eine blau emittierende Komponente bestimmt wird. Zudem führt der Konversionsansatz zu einer weniger komplexen Bauteilarchitektur und somit zu einer entsprechend einfacheren Herstellung. Überdies kann die Emissionsfarbe durch die Wahl der Leuchtstoffe in der Konversionsschicht eingestellt werden, ohne Änderungen im Diodenaufbau der zugrunde liegenden blauen OLED vorzunehmen.

Allerdings ist die Effizienz eines auf Lumineszenzkonversion beruhenden Bauteils durch die Effizienz der zugrunde liegenden blauen Lichtquelle gegeben. In der OLED-Technologie ist es bisher noch am schwierigsten Systeme zu entwickeln, die Licht im blauen Bereich des sichtbaren Spektrums emittieren. Im Rahmen dieser Arbeit wurde ein Ansatz demonstriert, bei dem sowohl Triplet- als auch Singulett Exzitonen in elektrophosphoreszenten OLEDs zur Erzeugung von blauem Licht nutzbar werden. Durch einen einfachen Zweischicht-Aufbau konnten diese Dioden in einem Lösungsmittel basierten Prozess hergestellt werden. Die erzielte Effizienz bewegt sich in der Größenordnung der Effizienzen, wie sie auch für blaue elektrophosphoreszente OLEDs auf Basis von kleinen Molekülen veröffentlicht wurden. Einflüsse auf die Effizienz dieser Diodenklasse wurden an Hand einer Reihe von Bauteilen mit unterschiedlich eingestelltem Ladungsträgergleichgewicht in der Licht emittierenden Polymerschicht untersucht. Neben dem Einfluss des Ladungsträgergleichgewichts konnte auch ein optischer, auf dem halbkavitativen Diodenaufbau beruhender Einfluss gezeigt werden. Dieser Interferenzeffekt,

der die wellenlängenabhängige und winkelabhängige Emission bestimmt, tritt dadurch auf, dass sich in einer OLED der Ort der Lichterzeugung in der Größenordnung der Wellenlänge des sichtbaren Lichts vor der reflektierenden Kathode befindet. Dieser Effekt wird durch die Lage der Emissionszone in der Licht emittierenden Polymerschicht bestimmt. Die simulationsgestützte Analyse von Emissionsspektren der untersuchten OLEDs ermöglichte die Lokalisierung der jeweiligen Lage der Emissionszone. Dadurch konnte der Einfluss des optischen Effekts auf die resultierende Effizienz quantifiziert werden. Auf dieser Untersuchung basierend wurde eine allgemeine Herangehensweise zur Effizienzanalyse von Bauteilen aufgezeigt, die es ermöglicht, den Einfluss des Ladungsträgergleichgewichts und den Einfluss des optischen Effekts auf die resultierende Bauteileffizienz getrennt zu bestimmen.

Wird auf der Licht emittierenden Substratseite einer OLED eine Konversionsschicht aufgebracht, kann eine Erhöhung der Lichtauskopplung aus dem Bauteil eintreten. Dieser Effekt beruht auf Lichtstreuung an Leuchtstoffpartikeln in der Konversionsschicht. Die Modifikation der Substratoberfläche ist ein bereits bekannter Ansatz, die Lichtauskopplung aus OLEDs zu verbessern. Dieser Ansatz beruht auf der Extraktion von Licht, das in der unmodifizierten OLED im Substrat wellengeleitet wird. Durch den halbkavitativen Aufbau der Diode - d.h. durch die gewählten Materialien, deren Schichtdicken und durch die Lage der Emissionszone – wird bestimmt, in welchem Maß Licht aus der OLED extern ausgekoppelt bzw. wellengeleitet wird. Bei der Anwendung einer Substratoberflächenmodifikation ist die Erhöhung der Lichtauskopplung das Verhältnis der externen Effizienzen des modifizierten und unmodifizierten Bauteils. In der vorliegenden Arbeit wurde gezeigt, dass die Erhöhung der Lichtauskopplung für eine gegebene Art der Substratoberflächenmodifikation vom Diodenaufbau abhängig ist. Folglich ist der Betrag der Lichtauskopplungserhöhung nicht ein präzises Maß zur Beurteilung einer Technik der Substratoberflächenmodifikation. Daher wurde eine allgemeine Methode zur Bewertung von Substratoberflächenmodifikationen für die Lichtauskopplung aus OLEDs eingeführt, welche unabhängig von der Diodenarchitektur ist. Das Verhältnis der insgesamt aus dem modifizierten Bauteil in Luft abgegebenen Lichtleistung zur Lichtleistung, die von der aktiven Diodenschicht in das Substrat eingekoppelt wird, stellt einen genaueren Parameter für die Beschreibung der Wirksamkeit einer Substratoberflächenmodifikation dar. Im Idealfall wäre dieses Verhältnis gleich 1. Dies entspräche einer Technik, die die Wellenleitung im Substrat vollkommen unterdrücken würde. Die Beschreibung der Wirkung nach der vorgestellten Methode ermöglicht nicht nur verschiedene Techniken der Substratoberflächenmodifikation zu vergleichen, sondern liefert

auch ein analytisches Maß für die weitere Verbesserung der jeweiligen Techniken. Die Bewertungsmethode wurde experimentell an grünen elektrophosphoreszenten OLEDs verschiedener Bauteilarchitekturen demonstriert. Dabei wurden die Substratoberflächen dieser OLEDs mit einem prismatischen Film modifiziert.

Überdies belegen die Ergebnisse aus Experimenten und optischer Modellierung klar, dass die Extraktionseffizienz von der Diodenarchitektur und der Lage der Emissionszone abhängig ist. Dies steht im Kontrast zur weit verbreiteten Annahme, dass die Extraktionseffizienz aus OLEDs ohne Substratoberflächenmodifikation unabhängig von der Diodenarchitektur $\approx 22\%$ beträgt. Folglich könnten Abschätzungen der internen Quanteneffizienz ohne Berücksichtigung der Diodenarchitektur zu falschen Schlussfolgerungen führen.

Ferner wurde aufgezeigt, dass die Erhöhung der Lichtauskopplung durch eine gegebene Lichtauskopplungstechnik von der Wellenlänge abhängt. Dieser Umstand kann zu Änderungen im Emissionsspektrum nach dem Modifizieren der Substratoberfläche von breitband-emittierenden OLEDs führen. Folglich sollte beim Abstimmen des Emissionsspektrums im Entwicklungsprozess von weißen OLEDs die optische Interaktion der verwendeten Substratoberflächenmodifikation mit der OLED berücksichtigt werden.

Weiterhin erfolgte eine optische Analyse von Kversions-OLEDs. Dazu wurden die in solchen Bauteilen auftretenden physikalischen Prozesse in einer Raytracing-Simulation abgebildet. Die Herangehensweisen zur Bestimmung aller relevanten Eingangsgrößen des der Simulation zugrundeliegenden Modells wurden an einem blauen Polymer-OLED Panel und einer Reihe Konversionsschichten demonstriert. Bei der Herstellung der Schichten wurde YAG:Ce³⁺ Pulver (Yttrium-Aluminium-Granat dotiert mit Cer) als Konversionsleuchtstoff verwendet. Eine Überprüfung der Simulation wurde durch den Vergleich aus Raytracing-Berechnungen erhaltenen Vorhersagen mit experimentellen Daten vollzogen. In Übereinstimmung mit früheren Arbeiten auf dem Gebiet zeigten sowohl experimentelle Ergebnisse als auch Simulationen, dass das Aufbringen einer Konversionsschicht auf dem Substrat zu einer Erhöhung der Anzahl der insgesamt in das Umgebungsmedium ausgekoppelten Photonen führen kann. Hinsichtlich der Konzentration des Leuchtstoffs in der Konversionsschicht bzw. der absoluten Schichtdicke wurde ein Maximum in der Auskoppelleffizienz in einem bestimmten Bereich der normierten Schichtdicke festgestellt (die normierte Schichtdicke wurde als das Produkt aus der Volumenkonzentration und der absoluten Schichtdicke definiert). Im Bereich geringerer normierter Schichtdicken findet durch die geringe Lichtstreuung an den Leuchtstoffpartikeln keine effektive Unterdrückung

der Wellenleitung im Substrat statt, während im Bereich hoher normierter Schichtdicken die mit Absorptionsverlusten verbundene Rückstreuung in die aktiven Schichten der OLED überwiegt. Das Maximum der Auskoppel-effizienz ist durch die Balance beider Effekte gegeben.

Allerdings ist in einer Konversions-OLED die Leuchtstoffkonzentration bzw. die Dicke der Leuchtstoffschicht nicht freiwählbar sondern durch den Zielfarbort bestimmt. Im optimalen Fall wird der für das Erreichen des Zielfarborts notwendige Anteil an Photonen konvertiert, während gleichzeitig die Lichtstreuung an den Leuchtstoffpartikeln zu einer effizienten Erhöhung der Lichtauskopplung führt. Diese Balance ist durch das Verhältnis zwischen Streuung und Absorption an den Leuchtstoffpartikeln gegeben. Gemäß der MIE-Theorie wird dieses Verhältnis durch die Größenverteilung der Leuchtstoffpartikel bestimmt. Mittels Raytracing-Simulation wurde die Steigerung der Lichtauskopplung durch die Konversionsschicht für eine Reihe von Partikelgrößenverteilungen analysiert. Die Ergebnisse aus der Untersuchung legen eine sorgfältige Wahl des Leuchtstoffpulvers nahe, da die Partikelgrößenverteilung einen entscheidenden Einfluss auf die Effizienz des Bauteils am Zielfarbort hat. Allerdings ist es schwer möglich, generelle Richtlinien für eine optimale Partikelgrößenverteilung zu finden, da für jeden Einzelfall der Zielfarbort und die optischen Konstanten des Leuchtstoffs und des Matrixmaterials der Konversionsschicht zu berücksichtigen sind. Dennoch sind Fallstudien für bekannte, charakterisierte Leuchtstoffe möglich. Diese Studien können die Entwicklung von effizienten Dioden mit dem gewünschten Zielfarbort ermöglichen. Das Modell kann überdies auch auf anorganische Lumineszenzkonversions-LEDs übertragen werden, bei denen die Konversionsschicht auf den LED-Chip aufgedruckt ist.

Ferner wurde mit Hilfe der Simulation der Einfluss der effektiven Reflektivität der zugrunde liegenden blauen OLED als weiterer Einfluss auf die externe Effizienz von Konversions-OLEDs untersucht. Für das Erzielen einer optimalen Effizienz sollte bei der blauen OLED beispielsweise durch eine geeignete Wahl des Kathodenmaterials eine möglichst hohe Reflektivität erreicht werden. Im Bereich der Reflektivität, der für OLEDs auf Basis der Bottom-Emitter Architektur typisch ist, hat eine geringe Wertänderung einen signifikanten Einfluss auf die externe Effizienz des gesamten Konversionsbauteils.

Überdies wurde die Abhängigkeit der Emissionsfarbe vom Blickwinkel untersucht. Die experimentellen Ergebnisse und Simulationsergebnisse zeigten, dass sich bei einer Konversions-OLED die Emissionsfarbe mit dem Blickwinkel ändert. Die winkelabhängige Intensitätsverteilung des in die Konversionsschicht eingekoppelten Lichts führt im

Zusammenspiel mit der vom Einkoppelwinkel abhängigen mittleren Absorptionswahrscheinlichkeit in der Konversionsschicht zu einer Emission mit höherem Blauanteil bei kleinen Winkeln in Bezug zur Substratnormalen. Zur Abschwächung dieses Effektes, d.h. zur Homogenisierung der Emissionsfarbe über den Blickwinkel, wurde ein neuartiger Ansatz vorgeschlagen, dessen Durchführbarkeit an Hand blau emittierender fluoreszenter OLEDs auf Basis kleiner Moleküle demonstriert wurde. Durch gezielte Manipulation der von der OLED gebildeten optischen Kavität wurde die winkelabhängige Intensitätsverteilung so gerichtet, dass die Emission bei höheren Winkeln im Bezug zur Substratnormalen deutlich verstärkt wurde. Dieses Vorgehen ist konträr zur üblichen Bauteiloptimierung, bei der die Emission in einen möglichst kleinen Raumwinkelbereich gerichtet wird, um Verluste durch Totalreflexion an der Grenzfläche vom Substratglas zur Luft zu minimieren. Die Erhöhung der Intensität bei höheren Winkeln wirkte der höheren Absorptionswahrscheinlichkeit bei höheren Einkoppelwinkeln in die Konversionsschicht entgegen und führte somit zu einer homogenen Emissionsfarbe über den Blickwinkel. Gleichzeitig konnte gegenüber einem Konversionsbauteil mit herkömmlich optimierter blauer OLED keine Verminderung der externen Effizienz festgestellt werden. Dies ist auf die Lichtstreuung an Leuchtstoffpartikeln zurückzuführen, welche die bei einer OLED ohne Konversionsschicht auftretenden Verluste durch Totalreflexion an der Grenzfläche vom Substratglas zur Luft minimiert.

Abschließend wurde die Umsetzung des Konversionskonzeptes in der OLED-Technologie erörtert. Die Realisierung von Konversions-OLEDs wird von der zukünftigen Entwicklung von hoch effizienten blauen elektrophosphoreszenten OLEDs und der Verbesserung deren Langzeitstabilität abhängen. Weiterhin ist die Entwicklung von neuartigen Leuchtstoffen notwendig, welche über die passenden Absorptions- und Emissionsspektren verfügen, um im Zusammenspiel mit einer hellblau emittierenden OLED weißes, für Beleuchtungsanwendungen geeignetes Licht zu generieren. Die Anwendung von Konversions-OLEDs wird sich nicht auf Beleuchtung beschränken; das Konversionskonzept ist auch besonders geeignet um flächige Symbol-Signalleuchten zu realisieren, die verschiedenfarbig leuchtende Flächenanteile aufweisen. Dieser Ansatz ist bedeutend effizienter als eine Realisierung auf Basis einer weißen Lichtquelle, die mit flächig strukturierten Farbfiltren versehen ist.

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Liste der Veröffentlichungen

In den folgenden Publikationen wurde ein Teil der Ergebnisse dieser Arbeit bereits veröffentlicht:

- (1) *"Highly efficient white organic light-emitting diode"*, B. Krummacher, V. Choong, M. Mathai, S.A. Choulis, F. So, F. Jermann, T. Fiedler, and M. Zachau, Applied Physics Letters 88, 113506 (2006).
- (2) *"Highly efficient solution processed blue organic electrophosphorescence with 14 lm/W luminous efficiency"*, M. Mathai, V. Choong, S.A. Choulis, B. Krummacher, and F. So, Applied Physics Letters 88, 243512 (2006).
- (3) *"Influence of charge balance and micro cavity effects on resultant efficiency of organic light emitting devices"*, B. Krummacher, M. Mathai, V. Choong, S.A. Choulis, F. So, and A. Winnacker, Organic Electronics 7 (2006).
- (4) *"General method to evaluate substrate surface modification techniques for light extraction enhancement of organic light emitting diodes"*, B. Krummacher, M. Mathai, V. Choong, S.A. Choulis, F. So, and A. Winnacker, Journal of Applied Physics 100, 054702 (2006).
- (5) *"OLED lighting – light where it never has been before"*, M. Klein, K. Heuser, F. Schindler, B. Krummacher, T. Dobbertin, R. Pätzold, and C. Gärditz, Proceedings of SPIE – Vol. 6486 Light-Emitting Diodes: Research, Manufacturing, and Applications XI, K. P. Streubel, H. Jeon, Editors, 64860E (2007).
- (6) *"Light Extraction From Solution-Based Processable Electrophosphorescent Organic Light-Emitting Diodes"*, B. Krummacher, M. Mathai, F. So, S.A. Choulis, and V. Choong, Journal of Display Technology 3, 2 (2007).
- (7) *"Recent progress in solution processable organic light emitting devices"*, F. So, B. Krummacher, M. Mathai, D. Poplavsky, S.A. Choulis, and V. Choong, Journal of Applied Physics 102, 091101 (2007).
- (8) *"Optical analysis of down-conversion OLEDs"*, B. Krummacher, M. Klein, N. von Malm, and A. Winnacker, Proceedings of the SPIE - Vol.6910, 691007-1-17 (2008).

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Danksagung

An dieser Stelle möchte ich mich bei den Personen bedanken, die zum Gelingen dieser Arbeit beigetragen haben.

An erster Stelle möchte ich mich bei Herrn Professor Albrecht Winnacker für die Betreuung der Arbeit, die zahlreichen fachlichen Diskussion sowie die vielen weiterführenden Anregungen danken. Herrn Professor Rudolf Weißmann gilt mein Dank für die Übernahme des Zweitgutachtens und die damit verbundenen Mühen.

Für das mir entgegen gebrachte Vertrauen bedanke ich mich bei Dr. Karsten Heuser, Dr. Alfred Felder und Dr. Homer Antoniadis, die die Idee einer Doktorandenstelle mit Tätigkeit auf beiden Seiten des Atlantiks hatten. Ein besonderes Dankeschön gilt auch Dr. Markus Klein und Dr. Bernhard Stapp für die damals unerwartete Möglichkeit nach dem Aufenthalt bei OSRAM Opto Semiconductors in San Jose, CA, die Arbeit am Standort in Regensburg fortzuführen.

Ebenso möchte ich mich bei meinen kalifornischen „supervisors“ Dr. Franky So und Dr. Vi-En Choong bedanken, die mich herzlich in ihrem Team aufgenommen haben. Trotz ihres dichten Terminplanes hatten sie immer ein offenes Ohr für mich und nahmen sich die Zeit für zahlreiche Diskussionen, die durch ihren reichen Erfahrungsschatz geprägt waren.

Vielen Dank gilt Dr. Florian Schindler für die vielen fruchtbaren Diskussionen, die fachlichen Anregungen und für die gute Zusammenarbeit während der Aufbauphase der OLED-Aktivitäten in Regensburg.

Herzlich bedanke ich mich bei dem gesamten OSRAM Opto Semiconductors-Team in San Jose für die Unterstützung und das harmonische Arbeitsumfeld. Namentlich sein hier meine mit-“group members“ Dr. Stelios Choulis, Dr. Mathew Mathai und Dr. Dmitry Poplavski erwähnt, welche stets für eine angenehme und kollegiale Atmosphäre, sorgten - sei es bei der Arbeit oder bei diversen gemeinsamen Freizeitaktivitäten wie gemeinsame Ausflüge, Abendessen oder Absacker im „Molly Mc Gee’s“.

Großen Dank geht an meine Regensburger Kollegen im „Converter-On-OLED“- Projekt Dr. Norwin von Malm und Manfred Url, mit denen es viel Freude bereitet hat gemeinsam auf dem gleichen Gebiet tätig zu sein.

Ein besonderes Dankeschön den Erlanger Kollegen Dr. Arvid Hunze, Dr. Dirk Buchhauser, Dr. Christoph Gärditz, Dr. Ralph Pätzold und Sabine Herder von SIEMENS CT für die gute Zusammenarbeit und für die Unterstützung während der Einarbeitungsphase.

Bedanken möchte ich mich bei den Regensburger Kollegen Dr. Kirstin Petersen, Dr. Dominik Eisert, Dr. Jörg Strauss, Dr. Bert Braune und Sebastian Glaser sowie bei den Münchner Kollegen Dr. Martin Zachau, Dr. Frank Jermann, Dr. Dirk Berben von der OSRAM GmbH für ihre Diskussionsbereitschaft, die Bereitstellung der Phosphore und deren optogeometrische Parameter sowie die Hilfe bei der Probenanfertigung.

Bei den Mitgliedern des OLED-Teams bei OSRAM Opto Semiconductors in Regensburg möchte ich für das angenehme Betriebsklima und die jederzeit vorhandene Hilfs- und Diskussionsbereitschaft bedanken, insbesondere bei Dr. Britta Göötze, Dr. Nina Riegel, Heidi Berghausen, Sabine Lorenz, Dr. Karsten Diekmann, Dr. Thomas Dobbertin, Dr. Michael Fehrer, Heiko Heppner, Egbert Höfling, Andrew Ingle, Dr. Arndt Jäger, Dr. Erwin Lang und Dr. Tilman Schlenker. Ganz besonders danke ich mich meinen beiden Kollegen und Freunden Martin Wittmann und Simon Schicktanz für den notwendigen Ausgleich bei zahlreichen Unternehmungen in der Freizeit und für die Hilfe beim Einleben in Regensburg.

Meinen Mitdoktoranden Riikka Suhonen, Stefan Seidel, Oliver Weiß und Ralf Krause danke ich für die gute Zusammenarbeit, fachliche und außerfachliche Diskussionen und Aktivitäten.

Bei den Mitarbeitern am Lehrstuhl Werkstoffe der Elektrotechnik bedanke ich mich für ihre Diskussions- und Hilfsbereitschaft, insbesondere bei Dr. Miroslav Batentschuk und Dr. Matthias Bickermann, sowie bei Frau Knerr und Frau Baumer aus dem Sekretariat für die Erledigung aller organisatorischen Angelegenheiten.

Herzlich bedanke ich bei meiner Mutter, bei meinen Brüdern Marcus und Florian, bei meinen Freunden und ganz besonders bei meiner Freundin Anja für ihre Geduld, die Unterstützung und nicht zuletzt für den notwendigen Ausgleich.

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