OVPD Coating Technology for the Processing of Efficient and Long-Lived OLED Luminaires

Von der Fakultät für Elektrotechnik und Informationstechnik der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation

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<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CCT</td>
<td>correlated color temperature</td>
</tr>
<tr>
<td>CFL</td>
<td>compact fluorescent lamp</td>
</tr>
<tr>
<td>CGL</td>
<td>charge generation layer</td>
</tr>
<tr>
<td>CIE</td>
<td>Commission International De L'eclairage</td>
</tr>
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<td>CQS</td>
<td>color quality scale</td>
</tr>
<tr>
<td>CRI</td>
<td>color rendering index</td>
</tr>
<tr>
<td>CV</td>
<td>cyclovoltammetry</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>EL</td>
<td>emission layer</td>
</tr>
<tr>
<td>ETL</td>
<td>electron transport layer</td>
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<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
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<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GDP</td>
<td>gross domestic product</td>
</tr>
<tr>
<td>HIL</td>
<td>hole injection layer</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTL</td>
<td>hole transport layer</td>
</tr>
<tr>
<td>HV</td>
<td>high vacuum</td>
</tr>
<tr>
<td>IC</td>
<td>internal conversion</td>
</tr>
<tr>
<td>IPES</td>
<td>inverse photoemission spectroscopy</td>
</tr>
<tr>
<td>IQE</td>
<td>internal quantum efficiency</td>
</tr>
<tr>
<td>ISC</td>
<td>intersystem crossing</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
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<tr>
<td>LED</td>
<td>light emitting diode</td>
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<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light emitting diode</td>
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<tr>
<td>OVPD</td>
<td>organic vapor phase deposition</td>
</tr>
<tr>
<td>SCLC</td>
<td>space charge limited current</td>
</tr>
<tr>
<td>SSL</td>
<td>solid-state lighting</td>
</tr>
<tr>
<td>TCO</td>
<td>transparent conductive oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TTA</td>
<td>triplet-triplet annihilation</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>VTE</td>
<td>vacuum thermal evaporation</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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1 Introduction

One glance from space on planet earth at night impressively shows the extent of artificial illumination. This view clearly visualizes the power of human-made illumination, revealing information from population density to wealth.

Our active life is mostly spent under artificial illumination. The availability has been and is an integral part of our cultural and economic development. At present, with inexhaustible, risk-free and economic energy sources far away from realization, the value of electrical energy becomes obviously clear. Even in highly developed countries, people strive to consume more light and are forced to use illumination more intelligently and to supply it more efficiently. Worldwide, with most people living in emerging countries, the total amount of consumed light is increasing fast.

From their invention, inefficient incandescent lamps play a major role in lighting. During the last decades, great effort has been invested in new light sources suitable for general illumination. The most known in residential environment are compact fluorescent lamps (CFL). However, CFL have not achieved a market penetration which would have threatened incandescent lamps. Systematic problems, like unsatisfactory marketing, hazardous substances, limited light quality and poor switching comfort have prevented a sustainable success.

In recent years, solid-state lighting (SSL) is a new market-relevant alternative growing at high speed. Inorganic blue light emitting diodes (LED) based on InGaN combined with a yellow phosphor are powerful and efficient enough to compete with CFL. Close to being competitive in terms of overall cost, white light emitting LED lamps can be bought in hardware stores, even having a classical E27 socket and bulb design.

Nevertheless, some lighting applications can only be insufficiently, or cannot be covered at all by inorganic LED lamps, but probably by organic light emitting diodes (OLED). OLED are based on a variety of organic molecules with a set of properties, allowing the vision of flexible, transparent and extremely thin lamp designs which are no longer point, but area light sources. OLED can be processed out of a solution or in a vacuum process. To be competitive with inorganic LED, many issues concerning efficiency, lifetime and cost of mass production have to be solved and are being heavily investigated presently.
1. Introduction

Having mostly completely different properties compared to inorganic semiconductors, the theoretical description of organic semiconductors and OLED is intensively researched on, but still not well understood. Complex organic layer stacks suitable for OLED lamps are largely developed and reviewed empirically.

Depending on their molecular mass, organic semiconductors can be divided into polymers and small organic molecules. Polymers are mostly processed out of a solution while small organic molecules are deposited via a vacuum-based process. This work focuses on small organic molecules.

At present, from laboratory tools to mass production equipment, small organic molecules are mostly deposited via a high vacuum (HV) based process. A lab-scale vacuum thermal evaporation (VTE) tool can be constructed fast and is relatively inexpensive. Therefore, it is the research tool of choice. As a consequence, the accumulated knowledge intrinsically favors the same technology to be scaled-up for mass production.

This work instead investigates the potential of an alternative process technique known as organic vapor phase deposition (OVPD) to fabricate white OLED suitable for general illumination. OVPD was invented by S. R. Forrest at Princeton University and licensed to Universal Display Cooperation [1]. Lab-scale OVPD tools having at least the same capability compared to lab-scale VTE tools are mechanically and electronically more complex and therefore more expensive. As a result, only a few research tools are available worldwide and process knowledge about OVPD OLED is limited. Therefore, it is aspired to enhance the throughput of the processing equipment to increase the number of experiments possible. In OVPD, organic materials are evaporated into a carrier gas (of e.g. nitrogen) and transported to a substrate by carrier gas flow. The system pressure is around 1 mbar. Therefore, in contrast to VTE it is easily possible to mix an unlimited number of organic materials at variable mixing-ratio during deposition. One goal of this work is to utilize OVPD-specific deposition properties to get new insights into the working mechanisms of the active layers of monochrome and white OLED.

No competitive white OVPD OLED has been presented before this work. Another goal of this work is to develop a white OVPD OLED with properties comparable to white VTE OLED. Besides this basic organic layer stack research, attention is always kept on the technical aspects related to the OVPD technology. Process stability and speed, flexibility and upscaling ability cannot be neglected when selecting which technology is advantageous for future mass production.

The following chapter gives a short introduction to the history and development of artificial illumination and the technical implications arising from political decisions
1. Introduction

Currently being made. Furthermore, the requirements artificial illumination has to fulfill are discussed, as well as the cost of light.

Basic physical properties of OLED are depicted thereafter. This includes the operation principle of OLED like charge carrier injection and transport as well as exciton formation and decay and the design of highly efficient emissive layers. The same chapter explains radiometric and especially photometric quantities of light sources and gives an introduction to the measurement setups utilized and constructed within this work. Furthermore, the chapter deals with degradation mechanisms, lifetime measurement and lifetime extrapolation of OLED. Finally, it compares concepts to realize white light emission by OLED and presents competing white VTE OLED efficiencies.

In chapter 4, an introduction to the VTE and OVPD technique is given followed by a short description of the process equipment utilized within this work.

Thereafter, the investigations leading to the development of a high-efficiency white OVPD OLED are described in detail. The development is broken-up into different fields of investigation, including the long-term stable injection of holes from the substrate, the p-doping of the hole injection and transport layer, the creation of an easy-to-adapt and stable phosphorescent emission layer and the presentation of a lifetime-improving concept. Finally, the acquired knowledge is combined to a white light emitting organic layer stack. The results are compared with theoretical calculations and loss channels are identified.

The concluding chapter summarizes the results and an outlook is given for future investigations.
2 Artificial Illumination

2.1 History of Lighting Cost and Efficiency

An extensive overview regarding the development of efficiency of artificial illumination, the total energy consumption of lighting, the cost of light and an assumption of the future development is given by Jeffrey Tsao in [2]. Photometric quantities like lumen are explained in chapter 3.2.

The total cost of light (measured in $/Mlmh=$ per megalumen hours) is a combination of the capital cost of the light source and the operating cost (electrical energy):

\[
CoL_{\text{total}} = CoL_{\text{capital}} + CoL_{\text{operating}}
\]

\[
\text{with } CoL_{\text{capital}} = \frac{CoS}{F \cdot \eta} \quad \text{and } CoL_{\text{operating}} = \frac{CoE}{\eta}
\]

\(CoL\): cost of light [$/Mlmh], \(CoS\): cost of light source [$], \(CoE\): cost of energy [$/MWh]

\(F\): luminous flux [lm], \(L_T\): lifetime, \(\eta\): luminous efficacy [lm/W]

Presently, according to [2], the total cost of light employing incandescent light bulbs is around 6 $/Mlmh and 1.3 $/Mlmh for fluorescent lamps (including CFL). Since 2008, the total cost of SSL solutions fell below the total cost of incandescent light bulbs and it is assumed that in 2011-2012 the total cost of fluorescent lamps will be achieved.

Because no end-consumer products are commercially available, an estimation of the cost of lamps employing OLED is very rough. The cost of light of OLED is probably several 100 to 1000 $/Mlmh [3] with the majority being capital costs.

It is shown in [2] that the cost of light from the 17th century till today has decreased from \(10^{1-5}\) $/Mlmh to around 1 $/Mlmh. This is due to the illumination efficiency, which has increased by 2 to 3 orders of magnitude, as well as the fact that the cost of energy decreased by 1 to 2 orders of magnitude. Furthermore, it is shown that through the centuries, 0.72% of the gross domestic product (GDP) has been spent for illumination. This is true for Great Britain in the 17th century, as well as for the developed or developing world in the 20th century. With decreasing energy costs, more light was consumed, concurrently, with increased efficiency of illumination, more light was consumed as well.
2. Artificial Illumination

Around 16% of the world’s electrical energy generation is consumed for lighting [2, 4] which is about 6.5% of the world’s primary energy consumption. If through the use of SSL, no matter if inorganic or organic, the efficiency of illumination increases, the implication is that less energy will be consumed. Rather, a discussion regarding the consumption perspective in developed and developing countries has to be started, possibly resulting in political decisions increasing the cost of energy. The luminous efficacy of commercially available lamps having an E27 socket is listed in Tab. 2.1.


<table>
<thead>
<tr>
<th>technique</th>
<th>luminous efficacy [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>incandescent</td>
<td>&gt;10</td>
</tr>
<tr>
<td>halogen</td>
<td>&gt;15</td>
</tr>
<tr>
<td>CFL</td>
<td>&gt;50</td>
</tr>
<tr>
<td>inorganic LED</td>
<td>&gt;60</td>
</tr>
</tbody>
</table>

The luminous efficacy of inorganic LED based lamps already exceed the one of CFL. An increase in illumination efficiency offers the option to increase the cost of energy without the need for the consumer to cut its consumption of light.

2.2 Lighting Requirements

2.2.1 Energy Efficiency in the European Union

European Union directive 2005/32/EG includes the possibility to define obligatory rules regarding the minimum environmental friendliness of energy-driven products in the European Union member states. On the basis of this directive, the European Union is investigating market relevance and potential energy savings of different product segments and authors regulations.

By regulation (EG) 244/2009 (“ban of incandescent lamps”), requirements of unfocussed light sources for general illumination are established and have to be fulfilled step-by-step. Different parameters, like efficiency, lifetime, off/on cycles and color temperature are regulated. Consequently, it will be prohibited to sell conventional incandescent light bulbs with an electrical power of more than \( \geq 7 \text{ W} \) after 1st of September 2012.

In the context of such political decisions, the demand for alternative and energy-efficient light sources will grow in future.
2.2.2 General Lighting by OLED

Suitable for general illumination, first large-area lamps based on OLED should fulfill the specifications listed in Tab. 2.2 [6].

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luminance</td>
<td>&lt;5000 cd/m²</td>
</tr>
<tr>
<td>Lifetime</td>
<td>&gt;5000 h</td>
</tr>
<tr>
<td>Luminous efficacy (without outcoupling enhancement)</td>
<td>&gt;20 lm/W</td>
</tr>
<tr>
<td>Luminous efficacy (with outcoupling enhancement)</td>
<td>&gt;40 lm/W</td>
</tr>
<tr>
<td>Color temperature</td>
<td>2800 K</td>
</tr>
<tr>
<td>CIEu,v stability (1-10 kcd/m²)</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

In early commercially available products (like designer lamps made for an exclusive niche market), a luminous efficacy of 20 lm/W will be acceptable, but the efficacy has to be increased at a high rate to compete with inorganic SSL and to be successful in the general lighting market.

To replace a conventional incandescent light bulb of 60 W, which can emit 700 lm, the active area of an OLED would have to be 450 cm² at a luminance of 5000 cd/m². To reduce the capital (manufacturing) cost per lm, it would be advantageous to increase the luminance even further. On the other hand, an OLED should be a glare-free (≤10,000 cd/m²) light source and by increasing the luminance further, the lifetime will be decreased and the more complex it will be to cool the devices sufficiently.

It is also worth noting that large-area light sources like OLED in most cases will have the feature to not only be a replaceable light source but a complete luminaire. The efficiency of OLED as a light source or integrated into a luminaire will in this case be the same. This implies, however, that at the end of the OLED lifetime, the entire luminaire has to be recycled. Therefore, an OLED must have a higher lifetime compared to the accepted 1000 h of incandescent light bulbs today.
3 Physical Background and Characterization Methods

3.1 Basic Architecture and Operation of OLED

Depending on the required properties, different OLED architectures exist. The main differences result from the choice of the substrate (flexible or not) and the light outcoupling concept (bottom- or top-emitting or transparent). This work focuses on bottom-emitting OLED fabricated on glass substrates. The schematic architecture of a complete device is shown in Fig. 3.1 (left) and an assembled white OLED in Fig. 3.1 (right).

![Architecture schematic](image)

**Fig. 3.1:** Architecture of a bottom-emitting OLED (left) and assembled OLED module (PHILIPS Lumiblade 47 mm x 43 mm) (right).

The glass substrate is covered by a structured transparent conductive oxide (TCO) which forms the anode. Typically and in this work as well, indium tin oxide (ITO), which is sputtered on the glass substrate, is used as TCO. Next, the organic layers are deposited on the TCO. The deposition of organic materials is followed by that of a reflective cathode. Generally, aluminum (Al), silver (Ag) or a combination of both is used as cathode material. The substrate is encapsulated by a glass cover to protect the organic and inorganic layers from atmosphere. Water and oxygen which diffuse through the glue connection between the substrate and the cover glass are absorbed by a getter material (Fig. 3.1 (left)) to prevent the degradation of the cathode and organic layers (compare chapter 3.5).
The organic layers consist of different organic semiconductors having specialized functions (e.g., hole or electron conductor or emitter). A simple organic layer stack is shown in Fig. 3.2 (left), while the main mechanisms, which are necessary for light emission in an OLED, are shown in Fig. 3.2 (right).

Exemplarily, a hole transport layer (HTL), an emission layer (EL) and an electron transport layer (ETL) are shown in Fig. 3.2 (left). Explicitly, white OLED can have much more complex organic layer stacks. The important principles of light emission are (Fig. 3.2 (right)):

1. Injection of charge carriers from the electrodes into the organic layers (HTL/ETL).
2. Charge carrier transport in the organic layers.
3. Charge carrier trapping on emitter molecules with the creation of an excited molecule state (exciton) and possible diffusion of this exciton.
4. Decay of excitons accompanied by the emission of photons.

To realize light emission efficiently in one single organic layer is nearly impossible (the more properties have to be combined in one molecular design the more difficult), so the transition from single-layer to multi-layer devices with specialized organic materials was an important development step to realize efficient OLED [7].

Organic semiconductors utilized for OLED are essentially hydrocarbons. Depending on the size of the molecules and the length of the hydrocarbon chains, organic semiconductors are classified as polymers or small molecules. Polymers are suitable for deposition out of a solution, but cannot be evaporated under HV conditions because the evaporation temperature (due to their high mass) is above their degradation temperature [8]. In contrast, small molecules are suitable for evaporation under HV
conditions, but at the same time are mostly hardly soluble due to insufficient functionalized side groups. Within this work, only small-molecule organic semiconductors are processed. Depending on their function, special atoms (like heavy metals) altering the properties of the semiconductors can be incorporated into the molecular design \[9\]. The general molecular design is based on hybridized sp\(^2\) carbon atoms which form a conjugated \(\pi\)-electron system with on the molecule delocalized electrons. The energetic splitting of the bonding \(\pi\) and anti-bonding \(\pi^*\) molecular orbitals results in an energetic gap \[8\]. This energetic gap can match the photon energy of the visible spectrum and thus, organic semiconductors can be employed as light-emitting materials.

The energetic gap is formed out of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Due to the interaction and polarization effects of organic molecules in an amorphous organic layer, the HOMO (as well as LUMO) energies are distributed in a Gaussian density of states (DOS) \[10-11\]. With a gap between the HOMO and LUMO energy in the range of \(>2\) eV, at room temperature nearly no \((<10^{-10} \text{ cm}^3)\) thermally generated free charge carriers can be found in the LUMO.

Because of the non-existent translation symmetry in amorphous organic layers and the low van-der-Vaals interaction between the molecules, in contrast to inorganic semiconductors, no energetic bands are formed and the charge carriers are localized in the HOMO and LUMO on one molecule. Charge carrier transport is realized by a hopping process from molecule to molecule \[12\] and can be regarded as a redox-reaction. Due to the low mobility of undoped organic semiconductors \((10^{-7}-10^{-3} \text{ cm}^2/\text{Vs})\), the total organic layer thickness has to be kept very low \((50-100 \text{ nm})\) to achieve an acceptably low drive voltage.

### 3.1.1 Exciton Formation and Decay

Electron-hole pairs created on organic molecules have a relatively strong (up to 1.5 eV) binding energy and are localized on one molecule. The excited molecule state is therefore a Frenkel exciton. The formation, transfer, and decay of excitons are of essential importance for the luminous efficiency of OLED \[9\]. The main rule to be obeyed is spin conservation. The total spin of a two-electron system can either be \(S=0\) or \(S=1\). Following spin statistics results in four excited states. One state (with \(S=0\)) is termed singlet and three states (with \(S=1\)) are termed triplet. Due to spin conservation and a molecule ground state having \(S=0\), in general, only the singlet states decay radiatively, whereas the triplet states decay non-radiatively. If only the singlet states decay radiatively, the according organic molecules are termed singlet emitters (compare with organic material list in Tab. 4.1) and the radiation is termed fluorescence. In the
case in which the excitons are created by electrical excitation involving charge carriers with arbitrary spin, the ratio between the creation of singlet and triplet states is approximately 1:3. The internal quantum efficiency (IQE) of singlet emitters is therefore limited to 25% (due to additional creation of singlet states by triplet-triplet annihilation (TTA) processes, the IQE can in fact be higher [13]). By incorporating heavy metal atoms with a high atom number $Z$ such as iridium (Ir) or platinum (Pt) in emitter molecules, mixed singlet-triplet states can be created and the probability of a triplet state to decay radiatively increases [14-15], while the lifetime of the triplet state decreases (down to μs). If triplet radiation is possible, the according emitters are termed triplet emitters and their radiation is termed phosphorescence. The IQE of triplet emitters can be up to 100%.

At high triplet exciton density and due the long lifetime of triplet excitons, TTA processes can occur [16]. If two triplet excitons interact, one excited state relaxes non-radiatively to the ground state while the other one is converted to an excited singlet state. In phosphorescent OLED, in which the recombination zone is located in a small volume at e.g. interfaces, TTA is responsible for a decrease in the current efficacy (roll-off) with increasing luminance. The local triplet exciton density and thus the interaction can be lowered if an as broad as possible recombination zone is realized (compare chapter 6).

Energy transfer between different singlet or triplet states on one molecule is termed internal conversion (IC), while the energy transfer from a singlet to a triplet state is termed intersystem crossing (ISC). Energy transfer between molecules can occur by Dexter or Förster transfer mechanisms [17]. Förster transfer is a long-range ($\sim 1/R^6$, $\approx 10 \text{ nm}$) non-radiative dipole-dipole transfer, while Dexter transfer is a short range ($\sim e^{2R}$, $\approx 1 \text{ nm}$) electron exchange transfer. Singlet states can be transferred by Dexter or Förster transfer with a predominating Förster transfer in the case of a donor-acceptor spectral overlap. Triplet states are transferred by Dexter transfer [8].

### 3.2 Radiometric and Photometric Quantities

#### 3.2.1 Quantum Efficiency

The IQE defines how many photons are created per injected electrons. Different processes (exciton annihilation, exciton decay rate) reduce the IQE and not all of the emitted photons can leave the device (oucoupling efficiency) but are reflected at interfaces. The external quantum efficiency (EQE) is easily externally measurable by:
3. Physical Background and Characterization Methods

\[
\eta_{\text{EQE}} = \frac{\eta_{\text{phot}}}{\eta_e}
\]

\(\eta_{\text{phot}}\): number of emitted photons

\(\eta_e\): number of injected electrons

The EQE can be derived from a measured spectrum and helps to identify possible loss mechanisms in OLED. First, it has to be calculated how many photons are emitted:

\[
n = \int_{400\ \text{nm}}^{800\ \text{nm}} \frac{w(\lambda) \lambda}{hc} d\lambda \cdot \Omega \cdot A
\]

\(w(\lambda)\): measured spectrum \([W / (sr \cdot cm^2 \cdot nm)]\)

\(\Omega\): solid angle

\(hc\): Planck constant, \(c\): light speed

\(A\): emitting surface area

Assuming Lambertian emission:

\[
\Omega = \int_0^{\pi/2} \int_0^{2\pi} \cos \theta \sin \phi \ d\phi \ d\theta = \pi
\]

and divided by the number of electrons injected, the EQE can be calculated by:

\[
\eta_{\text{EQE}} = \int_{400\ \text{nm}}^{800\ \text{nm}} \frac{w(\lambda) \lambda}{hc} d\lambda \cdot A \cdot \pi \cdot e / I_{el}
\]

\(e\): elementary charge

\(I_{el}\): electrical current

3.2.2 Outcoupling Efficiency

By ray optics, the outcoupling efficiency \(\eta_{\text{out}}\) of a bottom-emitting OLED with a perfect mirror cathode can be estimated [18] to:

\[
\eta_{\text{out}} \approx \frac{1}{2n^2}
\]

\(n\): highest index of refraction

On substrates having a low-index of refraction \((n=1.5)\), an outcoupling efficiency of bottom-emitting OLED of about 20% [19] has been measured. Due to total reflection at the substrate/organic interface, light is captured in organic modes and due to total reflection at the substrate/air interface, light is captured in substrate modes.

A half-sphere \((n=1.5)\) attached to a substrate of low refractive index increases the outcoupling efficiency by a factor of 1.8 in [19]. Additionally, the outcoupling efficiency increased further by a factor of 1.4 if substrates (and a half-sphere) of high refractive index \((n=1.8)\) were utilized.
In this work, OLED are processed on low-index glass substrates without any outcoupling enhancement. Further information about different outcoupling approaches (internally and externally) can be found in [20]. An e.g. half-sphere attached to an OLED is termed external outcoupling enhancement, while e.g. scattering layers integrated into the organic layer stack of an OLED are termed internal outcoupling enhancement. Without any outcoupling enhancement, light which hits the substrate/air interface in a too oblique angle cannot be coupled out.

3.2.3 Chromaticity Coordinates and Luminous Efficacy

The Commission International De L'eclairage (CIE) is a worldwide organization which exchanges information in the scientific field of light, lighting and related areas. Standards in the field of lighting are set by CIE publications. Definitions of general photometric vocabulary can be found in [21]. Photometric calculations can be performed with PlotIVL software written during this work (refer to chapter 10.1.1).

This chapter gives a short overview of color perception and calculation algorithms. An extensive overview is given in [22-23]. The CIE chromaticity or color coordinates define the color of a light source. Naturally, the definition of color coordinates is derived from the color perception of the human eye. Two different kinds of electrochemical receptors can be found in a human eye: Rods and cones. With the majority being rods, rods can only detect photons around a wavelength of 510 nm, but are very sensitive and used for monochrome dark (scotopic) vision under low brightness levels. In contrast, and important for white light illumination, are the cones, which are sensitive at different wavelengths and used for day (photopic) vision. Three different kinds of cones, which are sensitive at 440 nm, 540 nm and 590 nm can be found in a human eye. All three different types of cones have a different sensitivity and based on the convolution of cone stimulation by incident light (tristimulus values), color perception is realized. For photopic vision, based on the tristimulus values, the CIE 1931 color-matching functions were derived by CIE (Fig. 3.3). The color coordinates utilized in this work are based on these color-matching functions.
The tristimulus values $X$, $Y$ and $Z$ can be calculated out of a given spectrum and the color-matching functions according to:

$$X = \int w(\lambda) x(\lambda) d\lambda, \quad Y = \int w(\lambda) y(\lambda) d\lambda, \quad Z = \int w(\lambda) z(\lambda) d\lambda$$

$w(\lambda)$: spectrum

$x(\lambda), y(\lambda), z(\lambda)$: color matching functions

Generally, the tristimulus values are projected to a 2-dimensional color coordinates space and if necessary an additional brightness value. The 2-dimensional color coordinates can be calculated out of the tristimulus values by:

$$x = \frac{X}{X + Y + Z}, \quad y = \frac{Y}{X + Y + Z}, \quad z = \frac{Z}{X + Y + Z}$$

$x, y, z$: color coordinates

If $x$ and $y$ are plotted in a color coordinates diagram, the color of a light source can be visualized (Fig. 3.4). Further information about color spaces, transformations and calculations can be found in [22-23].
Fig. 3.4: CIE 1931 color coordinates diagram and example color coordinate at (CIE_x=0.40, CIE_y=0.40).

Besides color perception, due to the different sensitivity of the receptors (rods as well as the different types of cones) versus wavelength, radiometric quantities cannot describe the brightness perception of a human eye. Rather, a radiometric spectrum has to be weighted with the sensitivity of the human eye. For day vision (photopic), the 1951 Judd-modified spectral luminous efficiency function [24] (eye sensitivity function) is used within this work (Fig. 3.5).
3. Physical Background and Characterization Methods

3.1 Spectral Photopic Luminous Sensitivity

The eye sensitivity function can be utilized to calculate the luminous flux of a given spectrum. A comparison of radiometric and photometric units can be found in Tab. 10.3. Furthermore, if the spectrum is normalized, the maximum possible luminous efficacy can easily be calculated. The maximum possible luminous efficacy is termed true luminous efficacy of a light source and is defined as the maximum of luminous flux the light source could emit per unit of electric power. Respectively, the true current efficacy and maximum of luminosity at a certain electric current can be calculated as well:

\[ \eta = c \int \varpi(\lambda) V(\lambda) \, d\lambda \]

- \( \varpi(\lambda) \): normalized spectrum
- \( V(\lambda) \): eye sensitivity function
- \( c: 683 \text{ lm/W for the true luminous efficacy} \)
- \( c: 487 \text{ cd/A for the true current efficacy} \)

It follows that for a monochromatic light source at 555 nm, a maximum luminous efficacy of 683 lm/W can be achieved.

3.2.4 Color Rendering Index

The color coordinates only define the color impression of a light source in direct view and different spectra can create the same color impression (metamerism). It follows that even if two light sources have the same color coordinates in direct view, their spectra can be different and thus, the spectra of reflected light of illuminated objects...
can be different as well. Depending on the light source, the illuminated object creates a different color impression. To describe a light source in terms of how well it represents the color of objects in illumination, the color rendering index (CRI) has been developed.

The light source to be investigated is compared with a black body radiator of the same correlated color temperature (CCT) utilizing 8 (or up to 14) different test samples. The differences in the reflected spectra of the samples are taken to calculate the CRI. An incandescent lamp at a CCT of 2856 K (CIE standard illuminant A) has a CRI of 99 [25] with 100 being the maximum value, while a fluorescent lamp can be as low as 50. A CRI of 80 is regarded to be the minimum for general illumination (as defined by the ENERGY STAR label of the US Department of Energy).

Note that the CRI defines the quality of modern light sources like inorganic LED insufficiently and the US National Institute of Standards and Technology (NIST) currently defines a new standard collaborating in part with CIE, the color quality scale (CQS) [26]. Specifically, the CRI of light sources which are not close enough to the black body curve can only be insufficiently calculated and different light sources with a different CCT can result in the same CRI.

3.2.5 In-Situ Spectrometer and Luminance Meter

Spectra are taken either by an Instrument Systems CAS 140CT spectrometer or an OceanOptics USB650 fiber optics spectrometer. The fiber optics spectrometer is utilized to record spectra directly after processing under nitrogen environment and before encapsulation. The setup which was installed is shown in Fig. 3.6.

![Fig. 3.6: In-situ glovebox characterization by a fiber optics spectrometer.](image_url)

To control and automate spectra recording, GSpec software was written (refer to 10.1.4). GSpec controls the spectrometer and power supply and records spectra at certain current density or luminance, visualizes color coordinates and calculates
efficiencies, so that the user immediately gets feedback about the processed organic layer stack.

For photometric measurements, a Minolta luminance meter LS-110 and calibrated photodiodes are used. OLED are measured in forward direction and Lambertian emission is assumed for photometric calculations. The Lambertian emission characteristic was verified with different OLED and detailed information can be found in [20]. Thereby, luminous flux can be calculated out of luminosity by:

$$F = I \int_{\phi=0}^{\phi=\pi} \int_{\theta=0}^{\theta=\pi/2} \cos \theta \sin \theta d\theta d\phi = \pi \text{sr} |I$$

where $F$: Luminous Flux [lm], $I$: Luminosity [lm/sr]

### 3.3 Charge Injection at Interfaces

The charge injection properties of the electrode/first organic layer interface are of great importance to guarantee a stable device operation. If the charge injection is deteriorated by operating time or due to operating conditions (e.g. temperature), the device characteristics (like color coordinates or homogeneous emission versus active area) most probably change significantly. To prevent a degradation of these interfaces, it is necessary to understand the mechanisms of charge injection.

The simplest model of charge injection from a metal into an organic semiconductor is shown in Fig. 3.7.

![Fig. 3.7: Different mechanisms of charge injection from a metal contact into the LUMO of an organic semiconductor if an injection barrier $\Phi_b$ is present.](image)

As a first approximation, the injection of exemplarily electrons from a metal into an organic semiconductor can be described as emission of electrons through a triangular potential barrier (outer electric field is applied in Fig. 3.7) [27]. In the case in which an
electron is thermally activated to overcome the injection barrier, the process is called thermionic emission. In the case in which the electron tunnels through the barrier starting at the metal’s Fermi level $E_F$, the process is called field emission. In between these two processes, a thermally activated tunneling injection known as thermionic field emission exists. This simple model of charge injection has to be extended comprehensively (e.g. applying the image charge potential effect [27]) to be consistent with experiments. Further theoretical information can be found in [8, 28-29], but interface injection theory involving organic semiconductors is still a developing field far away from the level of understanding achieved with inorganic semiconductors.

However, during the last years, a mixture of complex interface effects have been discovered and experimentally validated [30]. Recently, by ultraviolet (UPS), X-ray (XPS) and inverse photoemission spectroscopy (IPES), the energetic structure (HOMO and LUMO energies) of a complete OLED with doped injection layers was investigated sequentially in [31]. A bending of the HOMO/LUMO energies as well as a pronounced interface dipole at the contacts was found.

Fig. 3.8 summarizes and visualizes different effects and their influence on HOMO and LUMO energies as well as the vacuum level of a multi-layer OLED under operation.

At the cathode side of the device, an energy level bending of a doped injection and transport layer is shown. The bending of the energy level at the interface to the metal cathode enhances the injection of electrons. Inside the doped transport layer, nearly no electric field is present and the energy levels are flat. To enhance the injection of charge carriers or increase the conductivity of thick transport layers, electrical doping is applied often. In this work, the injection of electrons from the cathode is enhanced by doping the cathode/electron injection layer interface with Lithium (Li). The use of
reactive metals such as Li or Cesium (Cs) is a commonly applied method [32]. Alternatively, organic dopants can be utilized (Fig. 3.9).

**Fig. 3.9:** HOMO and LUMO energy of host and dopant in the case of organic p- and n-type doping.

In the case of organic dopants, a p-type dopant has a matching LUMO energy, so that an electron can be extracted from the HOMO of the host material, while an n-type dopant has a HOMO energy, which allows the supply of an electron to the LUMO of the host material. A comprehensive review about the doping of organic semiconductors can be found in [33].

In contrast to the doped ETL in Fig. 3.8, an undoped EL has tilted energy levels (charge carrier concentration too low to compensate the outer electric field) under operation. At the anode side of the device, the injection of holes is enhanced by a dipole layer (e.g. a self-assembled monolayer attached to the anode surface [34]) shifting the vacuum level and reducing the injection barrier. Specifically, the instability of such a dipole layer can deteriorate the injection of holes significantly changing the emission characteristics during operation. With a focus on the anode side of the device and the injection of holes, Fig. 3.10 compares three different mechanisms, which are suitable to enhance hole injection.

**Fig. 3.10:** Different mechanisms of hole injection at the anode to first organic layer interface: dipole layer (A), p-doping (B) and oxide buffer layer (C).
Additional to the creation of a dipole layer or p-doped injection layer, the injection of holes can be enhanced by the insertion of a thin oxide interlayer which can extract electrons out of the HOMO of the following organic layer via its conduction band (CB) (Fig. 3.10 (C)). A detailed description of this effect can be found in [35-36]. In chapter 5, based on the presented mechanisms, different concepts to stabilize charge carrier injection at interfaces are presented. Concurrently, the p-doping of OLED in an OVPD system is investigated.

### 3.4 Emission Layers Concepts

The design of the EL is one of the most important components to realize a highly efficient OLED. This chapter discusses EL concepts and answers the question how different phosphorescent emitters can be integrated into one EL.

To start with, two basic EL concepts are shown in Fig. 3.11.

**Fig. 3.11:** EL consisting of hole-conducting host and electron conductor being the emitter as well (A) and EL with two host materials and charge carrier trapping on emitter molecules (B).

The EL concept shown in Fig. 3.11 (A) is commonly used in simple monochrome fluorescent devices. The e.g. electron-conducting host material is concurrently the emitting molecule. In the case of different hole and electron mobilities and an accumulation of excess charges (e.g. holes) at the host/emitter interface, emitter molecules (apart from exciton formation) can be oxidized. This is a possible degradation mechanism (chapter 3.5.3). In Fig. 3.11 (B), a typical EL concept used in phosphorescent devices is shown. Holes and electrons are transported by different host materials, while charge carriers are trapped on special emitter molecules doped into one host material or across the interface of both materials. If the emitter is doped into both host materials, a so-called double EL is created. The double EL concept was
investigated in [37]. With a focus on phosphorescent emitters, the EL of Fig. 3.11 (B) is commonly used for monochrome devices (compare green OLED in chapter 6.2), but as soon as more than one type of emitter has to be integrated in the organic layer stack, the concept has to be extended.

In Fig. 3.12, two possibilities of how the EL of Fig. 3.11 (B) can be extended are presented. The requirement is that the emission of both emitters has to be stable with e.g. process variations, luminance, operating points and device temperatures. Both of the concepts shown are strongly dependent on the type of host materials and emitters utilized. Concept Fig. 3.12 (A) requires a suitable bipolar-conducting host material to spatially split the recombination zone, while the emission of the low triplet energy emitter of concept Fig. 3.12 (B) is realized by triplet exciton diffusion from the high triplet energy emitter. The triplet diffusion strongly depends on the emitter concentrations, as well as triplet energy, triplet lifetime, triplet density and consequently luminance, too. In the case of even small process variations (e.g. emitter concentrations), it is hardly possible to guarantee stable device properties. Due the dependence on triplet diffusion, in the case the operating point (luminance, device temperature) is changed, the device properties (color coordinates) most probably will change, too. How can the concept be improved and stable exciton generation on both emitters be realized?

In literature [38-40], the mixture of a hole- and electron-conducting host material has been investigated. In Fig. 3.13, the concept of a mixed-host EL is shown.
3. Physical Background and Characterization Methods

Fig. 3.13: Mixed-host EL doped with different emitters.

The hole- and electron-conducting host materials are mixed, while two different emitters are doped into the mixed host. Due to the mixture of host materials, holes can be transported to the emitter close to the cathode side of the EL, while at the same time electrons are transported in direction of the anode side of the EL by the opposite host. In an ideal, charge-balanced case, the exciton generation and recombination in a mixed-host EL is evenly distributed versus EL position (Fig. 3.14 (A)). This guarantees a broad recombination zone (low TTA) and an easy emission ratio tuning between the two emitters simply by changing the ratio of the emitter doped regions.

Fig. 3.14: Hole, electron and exciton density in mixed-host EL. Charge-balanced EL with constant exciton density versus EL position (A) and charge-imbalanced EL with high exciton density at anode side of the EL (B).

However, in the case that by e.g. changed injection properties, the mixed-host EL became charge-imbalanced, the emission would shift to exemplarily the anode side of the EL (Fig. 3.14 (B)). This would change the emission characteristics (like color coordinates) significantly and moreover, the device can suffer from increased triplet exciton quenching, if excitons diffuse in the adjoining charge transport layer of low triplet energy. Therefore, stable operation of a mixed-host EL OLED is to some extent
dependent on the operating point. In chapter 6, mixed-host EL and their advantages (as well as drawbacks) are investigated intensively and a new more stable mixed-host EL concept is developed.

To achieve a charge-balanced operation, the mixture ratio of the host materials can be tuned. As explained earlier, charge carrier transport is realized by hopping from molecule to molecule [12] (Fig. 3.15 (left)). The potential barrier between the molecules is to be thermally overcome, while the barrier is lowered due to an outer electric field (Poole-Frenkel effect [41]). If the density of transport molecules is changed inside a transport layer, the hopping probability (and mobility) can be changed as well (Fig. 3.15 (right)).

Fig. 3.15: Energy distribution of HOMO/LUMO in a Gaussian DOS (left) with hopping transport from molecule to molecule versus position.
Hopping transport at different density of transport molecules (right).

Generally, due to the low mobilities in organic semiconductors, a space charge limited current (SCLC) can be observed. In the case of a unipolar device, SCLC can be described by Mott-Gurney law (assuming no traps and no field-dependent mobility) [8]:

$$ J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3} $$

$\varepsilon$: permittivity of organic layer
$\mu$: mobility of charge carriers
$d$: thickness of organic layer
$V$: voltage

Even if a simple [42] or more complex [43] field-dependent mobility is considered, the SCLC can only be used to describe thicker single carrier type devices. When it comes to complete OLED and bipolar multilayer organic layer stacks with a thickness of below 100 nm, complex field- and temperature-dependent mobility effects generally prevent a simulation or prediction of device characteristics. A comprehensive analytical model has not yet been developed.
3. Physical Background and Characterization Methods

3.5 OLED Lifetime and Degradation

An overview about common OLED degradation types and underlying mechanisms can be found in [44]. The lifetime of specifically monochrome red OLED is investigated in chapter 7 and a new concept to improve it, is presented. This chapter discusses possible degradation mechanisms and strategies to prevent them. Lifetime-limiting factors can generally be divided into different categories depending on the type of degradation. The most important categories are:

- Dark spots (appearance of non-emissive spots in the active area which grow by time).
- Complete failure (no emission).
- Luminance decrease (Continuous decrease versus operating time at constant current).

The underlying mechanisms are explained in the following.

3.5.1 Appearance and Suppression of Dark Spots

The main mechanism resulting in non-emissive dark-spot appearance can be traced back to a degradation of the ETL/cathode interface. Water and oxygen can diffuse through small pinholes in the metal cathode layer towards the organic interface. This can result in a local delamination of the metal cathode and thus a deterioration of electron injection. Furthermore, at the ETL to metal cathode interface, reactive metals like Li or Cs are often utilized in combination with Al or Ag to enhance electron injection. In the presence of water or oxygen, they can undergo unwanted reactions (oxidation) preventing further injection of electrons.

Diffusion of water and oxygen as well as the related reactions occur in the on- as well as off-state of the OLED, but are accelerated thermally in the on-state. The encapsulation of devices prevents the appearance of dark spots and is a common method to separate the device from the surrounding atmosphere. Further information regarding this type of degradation mechanism can be found in [45].

3.5.2 Complete Device Failure

Short circuits are the main reason for a complete failure. During the processing of OLED, particles can be incorporated into the organic layers. The size of the particles can range from thinner to thicker than the total thickness of the organic layers. Depending on the conductivity of the particles and anomalies of the organic layers (and their local thickness) in their surrounding, the current density can increase locally in the on-state of the OLED. Due to the non-linear dependence of current density on organic layer thickness (compare equation (3.10)), a locally higher current density can
be caused easily by small thickness deviations of the organic layers. Consequently, the organic layers can heat up, melt and cause a short circuit. To prevent complete failures, the whole process of OLED manufacture should be as clean as possible in a suitable clean-room environment.

3.5.3 Luminance Decrease by Intrinsic Degradation

The continuous decrease of luminance with operation time at constant current is caused by intrinsic degradation. Several processes have been identified to be responsible for intrinsic degradation [44]. The effects are dependent on the exact organic layer stack and material composition and cannot be generalized. Often, a complex interplay between different organic materials in one or more organic layers can influence this type of degradation.

Each charge carrier transport process requires a molecule to undergo a redox-reaction. If such an e.g. already oxidized molecule is oxidized for a second time, the molecule can become unstable and bonds can break. As a consequence, a higher current density results in an accelerated degradation.

One major problem discussed in chapter 7 is the instability of organic materials against charge carriers and excitons. Exemplarily, in [46] the instability of cationic Alq₃ (electron conductor and emitter, compare Tab. 4.1) species, which can act as emission quenchers, was investigated.

If the glass transition temperature of the organic materials is exceeded, a change in the morphology of the organic layers and a degradation of the OLED becomes possible. This effect is defined as thermal degradation and can be prevented by a suitable cooling of the device or a limitation of the maximum power density.

Another mechanism causing intrinsic degradation is the deterioration of the hole injection at the ITO/organic interface [47]. In contrast to the continuously and homogenously decreasing luminance of the whole active area versus operation time, a local degradation of the hole injection results in an inhomogeneous luminance and possibly different color coordinates versus position of the active area. The stability of hole injection is investigated in chapter 5.

This work focuses on some of the described intrinsic degradation mechanisms and investigates their influence on OLED lifetime. Dark spots are prevented by encapsulation (more information about the quality of the encapsulation can be found in [45]) and the number of devices which completely fail is reduced by an as particle-free as possible process. The deposition tool is situated in a simple particle-reduced facility,
but the substrates are handled in down-flow boxes only. The down-flow boxes offer a class 100 (US-FED-STD-209E) clean-room environment.

3.5.4 Lifetime Definitions and Measurement Setup

Commonly, the lifetime of OLED is defined as the time until the luminance has decreased to 50% of the initial luminance at constant current. To extrapolate measured lifetime data, a stretched exponential decay function can be used [48]:

\[ L = L_0 e^{-\alpha t^\beta} \]

where:
- \( L \): initial luminance
- \( L_0 \): initial luminance
- \( \alpha, \beta \): constants

When extrapolating the lifetime, the luminance should have decreased to 60% of its initial value to achieve an extrapolation error of less than 10% [49].

In Fig. 3.16, one of the developed lifetime measurement stations is shown.

![Fig. 3.16: Lifetime measurement station showing an OLED in measurement position. (OLED bottom-side = emission side down)](image)

The OLED to measure is placed on a metal plate in which a hole is drilled. Light emitted by the OLED is collected by a photodiode which is mounted at the back of the metal plate. The amplification of the photocurrent can be changed to be able to measure a broad range of luminance. A constant-current power supply is integrated into the setup and a cover protects it from ambient light. The lifetime measurement station was designed to be stand-alone functional and easy to duplicate. Seven stations were built-up and the number can be extended if necessary.
The amplified photocurrent (monitored as voltage) as well as the drive voltage of the OLED is measured via a computer interface and supplied to GLife (chapter 10.1.5), a software program which was written during this work. GLife can be used to log measurement values and extrapolate them utilizing equation (3.11).

Another common way to calculate the lifetime of OLED at standard low luminance (e.g. 1000 cd/m²) is to measure the lifetime at a very high luminance (e.g. >10 000 cd/m²) and extrapolate it using the Coffin-Manson model [48]:

\[ L^n T_{1/2} = \text{const.} \]

- \( L \): luminance
- \( n \): acceleration factor
- \( T_{1/2} \): lifetime

The lifetime can be measured at a high luminance and extrapolated to a lower luminance if the acceleration factor \( n \) was determined beforehand.

The Coffin-Manson model can be extended to the form:

\[ p^n j^n T_{1/2} = \text{const.} \]

- \( p \): power density
- \( j \): current density

Instead of the luminance \( L \), the power density \( p \) and the current density \( j \) are used to extrapolate the lifetime. Both are main causes for intrinsic OLED degradation. The power density determines the temperature of the OLED and the current density determines the number of redox-reactions and recombination processes in the OLED. The effect of the current density can be non-linear if it is high enough to cause molecule degradation by e.g. double-oxidation processes.

In our group [50], the influences of the power density and current density were independently investigated. The setup of Fig. 3.16 was therefore extended to allow a pulsed-mode operation. In pulsed-mode operation, the drive current is no longer constant, but is switched off and on periodically. Consequently, by changing the ratio between the off and on state (in a period), the power density can be kept constant, while the current density can be changed and vice versa.

### 3.6 Concepts for White Emission

Different concepts exist to realize white emission by OLED. All of them are described well in literature, so that only an overview is given here. A more extensive description can be found in [37, 51].
Adopted from current white lamps based on inorganic LED, one possible approach is to utilize only blue-emitting OLED with some of the light being partially converted to yellow via phosphors. In summation, a white light impression can be created (Fig. 3.17 A). However, this approach is rather less promising for OLED due to the fact, that no long-lived highly-efficient phosphorescent blue emitters have been developed up to now.

![Different concepts](image)

**Fig. 3.17:** Different concepts to realize white OLED. A: Single blue EL. Blue light partially converted by a phosphor to yellow. B: Red-, green- and blue-emitting OLED horizontally separated (stripe design). C: Vertically stacked red-, green- and blue-emitting OLED connected via CGL. D: Red-, green- and blue-emitting layers integrated into one organic layer stack.

Alternatively, red, green and blue OLED can be arranged horizontally (Fig. 3.17 B) or vertically (Fig. 3.17 C). To separate the differently emitting OLED horizontally would require the realization of a stripe or dot design. The organic layer deposition and the control of the different colors would get complex and the effort and cost would increase. In the case when differently emitting OLED are stacked vertically, charge generation layers (CGL) [52-54] between the organic layer stacks of different emission color are necessary. Both concepts, horizontal stripes as well as CGL are prone to errors due their complexity.

Therefore, the integration of red, green and blue emitters into one multi-layer organic layer stack (Fig. 3.17 D) is chosen to achieve white-light emission by OLED in this work. Red and green emission is realized by phosphorescent emitters, which have the advantage of a high IQE and therefore high EQE at acceptable emitter lifetimes, while the blue emission is realized by a fluorescent blue emitter. As mentioned, until today no long-lived phosphorescent blue emitter has been synthesized. The combination of phosphorescent red and green and fluorescent blue emitters is termed hybrid.
3.6.1 100%-Efficient White Light

To calculate the maximum efficiency of a white light source, boundary conditions like the minimum acceptable CRI, the required CCT, the emission characteristics of the emitters (e.g., Gaussian peaks with a defined full width at half maximum (FWHM)), as well as the number of emitters have to be given. If the central wavelength (assuming Gaussian peaks) of the emission spectra and the relative power distribution are varied, the true luminous efficacy (chapter 3.2.3) of such a light source can be determined.

With the number of emission peaks (FWHM of 1 nm) set to 4, a CCT of 3000 K and a CRI of at least 90 according to [55], a true luminous efficacy of 408 lm/W can be calculated. Note that [55] had inorganic LED in focus and in regard to their emission characteristic, a FWHM of 1 nm was chosen. However, in the following, 408 lm/W is regarded as 100%-efficient for OLED as well. Generally, the higher the CRI, the lower is the true luminous efficacy and vice versa.

In Fig. 3.18, the eye sensitivity functions (chapter 3.2.3) as well as the central emission wavelengths of the 100%-efficient white light source are plotted into one graph. The eye sensitivity function \( V(\lambda) \) and the color matching function \( y(\lambda) \) in the green emission spectrum have the same shape.

![Fig. 3.18: Eye sensitivity functions and the emission peaks of a 100%-efficient white light source.](image)

It can be seen that the blue emission peak at 459 nm only contributes to the color coordinates of the white light source, but not to the luminance and thereby efficiency of the light source.

Later-on, it is shown that the blue emitter utilized is also the least efficient in terms of EQE. To be able to reduce the amount of photons generated by the blue emitter as far
as possible, the photons should be emitted in the maximum of the short-wavelength color matching function $z(\lambda)$, which is around 450 nm. The emission in the greenish-yellow region should be around the maximum (555 nm) of the eye sensitivity function $V(\lambda)$ and the emission in the red region should not exceed a wavelength of around 625 nm. Around 20% of the photons should be emitted in the blueish region, 40% in the greenish region and another 40% in the red region.

### 3.6.2 White OLED Reference Efficiencies

As reference for VTE-processed OLED, only hybrid white OLED with acceptable color coordinates in the proximity of the black body curve are chosen. At warm-white color coordinates, a luminous efficacy of 13.7 lm/W at 1000 cd/m² was achieved in [56]. Applying doped transport layers, a luminous efficacy of 23.3 lm/W at 1000 cd/m² and warm-white color coordinates can be found in [57]. None of the devices utilized an outcoupling enhancement.

Apart from scientific literature, different companies reported efficiencies around 50 lm/W at 1000 cd/m² and a CCT of 2700-3300 K [58]. All of them are hybrid devices and utilize thin external outcoupling structures like structured foils.

Probably, a hybrid device as well and for product development commercially available in small numbers is OSRAM’s ORBEOS OLED. According to the datasheet [59], at color coordinates of 0.46/0.42 and 1000 cd/m² 23 lm/W are achieved. The lifetime is stated with 5000 h at the same luminance.

When this work was started, the maximum luminous efficacy of hybrid white OVPD OLED was below 2 lm/W [37]. The concept for white light emission was based on the integrating approach (Fig. 3.17 D). The organic layer stack of the investigated OLED consisted of three separated EL. The fluorescent blue EL was situated at the anode side of the device, followed by a phosphorescent green and red EL.
4 Production Techniques and Equipment

4.1 Vacuum Thermal Evaporation (VTE)

Different kinds of deposition techniques are suitable to deposit layers of organic material with thicknesses in the \textit{nm} range homogeneously and reproducibly. Today, VTE utilizing HV environment (10^{-6} \text{ mbar}) is the most common technique for organic layer deposition. Organic materials are heated up and evaporated out of a crucible followed by a ballistic transport from the crucible to the substrate (Fig. 4.1 (left)). The crucibles are heated up to the required evaporation temperature for deposition and are cooled down again after deposition. The deposition rate is controlled by the source temperature and measured by a quartz crystal.

![Fig. 4.1: VTE basic setup (left). VTE linear sources and substrate transport (right).](image)

To realize a homogeneous layer thickness, it is necessary to keep a certain minimum distance between the evaporator and the substrate. Thereby, a trade-off between homogeneity and material usage is given. In most cases, the substrate is rotated during deposition.
The principle of VTE can be integrated into lab-scale tools as well as systems suitable for mass production. To process large-area substrates, in-line systems with linear sources are favorable (for more information compare [60]). In Fig. 4.1 (right), two linear sources with an overlap of their evaporation cones are shown. If both sources evaporate different materials simultaneously, the overlap realizes a mixture of two materials in a single organic layer. The substrates are transported through different HV chambers with different linear evaporator setups to create the complete organic layer stack of the desired OLED.

The more complex the organic layer stack, the more evaporation chambers are needed. This becomes especially complex if a repetition of the whole organic layer stack is required to fabricate stacked OLED.

4.2 Organic Vapor Phase Deposition (OVPD)

4.2.1 Basic Setup

Another deposition technique is OVPD. In contrast to a ballistic material transport in HV of a VTE setup, OVPD is based on a different mechanism of transport.

An inert carrier gas like nitrogen ($N_2$) flows around heated crucibles loaded with organic materials (Fig. 4.2) and transports the evaporating organic materials to a (cooled) substrate, on which the molecules are deposited. The carrier gas is further transported to a pump, which holds the pressure in the deposition chamber at a constant level of around 1 mbar. The deposition rate can easily be adjusted by mass flow controllers (MFC) which control the flow of carrier gas. Theoretically, an unlimited number of organic materials can be mixed by mixing the carrier gas flows prior to deposition. By adjusting the MFC, the mixture ratio can be changed fast, continuously and reproducibly.

![Fig. 4.2: OVPD basic setup.](image)
In contrast to a VTE system (slow deposition rate change due to the dependence on source temperature, restricted number of materials mixable due to the dependence on evaporator setup), an OVPD system offers the possibility to deposit and investigate sophisticated mixtures (including mixture profiles) in the e.g. active layer of OLED (compare chapter 3.4 and chapter 6).

In an early attempt [61] in 1995, the growth of non-linear optical crystals in an OVPD system under atmospheric pressure was evaluated. The first OVPD OLED under low pressure conditions can be found in [62]. A review about low-pressure OVPD and the growth mechanisms of non-linear optical crystals and amorphous organic layers for photonic applications can be found in [63].

4.2.2 Evaporation Regimes

Two regimes of evaporation are described [64]. The organic material partial pressure in the source can reach equilibrium (i.e. partial pressure = vapor pressure) at higher temperatures and lower source flows. Consequently, the rate of organic material leaving the source is proportional to the organic material vapor pressure and the carrier gas flow. At lower source temperatures and higher carrier gas flows, the source operates in the kinetic mode. All material evaporating in the source is carried away by the carrier gas. The rate of organic material leaving the source is independent of the carrier gas flow.

If the ideal gas law is considered to describe the sublimed material, the evaporation rate (organic material exiting the source) results in:

\[ r = Q \frac{P}{RT_s} \]

\( r \): evaporation rate

\( Q \): carrier gas source flow

\( P \): organic material partial pressure

\( R \): universal gas constant

\( T_s \): source temperature

The equilibrium vapor pressure \( p_{eq} \) of the organic material at higher source temperatures can be written as:

\[ p_{eq} = p_0 e^\frac{\Delta H_s}{RT_s} \]

\( p_0 \): empirical constant

\( \Delta H_s \): evaporation enthalpy

and the evaporation rate (of organic material inside the source) equals:
\[ r_{eq} = k_{evap} p_{eq} \]

\[ k_{evap} \text{: kinetic factor for evaporation} \]

Fig. 4.3 visualizes the vapor pressure for two different organic materials with different \( \Delta H_s \), where \( \Delta H_s^a < \Delta H_s^b \).

\[ \text{Fig. 4.3: Vapor pressure versus evaporation temperature for different } \Delta H_s. \]

With the rate of condensation \( r_{\text{cond}} \) being proportional to the organic material partial pressure (inside the source) \( p \):

\[ r_{\text{cond}} = k_{\text{cond}} p \]

and \( r = r_{\text{evap}} - r_{\text{cond}} \) as well as (4.1):

\[ \frac{p}{p_{eq}} = \frac{k_{\text{evap}}}{\frac{Q}{RT_s} + k_{\text{cond}}} \]

\[ (4.5) \]

can be derived. In the case in which no or only a small carrier gas source flow is considered, \( k_{\text{evap}} = k_{\text{cond}} = k \) follows. If (4.1) and (4.5) are combined, the evaporation rate results in:

\[ r = \eta \cdot \frac{Q}{RT_s} \cdot \frac{1}{1 + \frac{Q}{kRT_s}} p_{eq} \]

\[ (4.6) \]

\( \eta \): geometry factor
The system geometry factor was added and investigated in [65]. At small carrier gas flow (source in equilibrium) the organic material exiting the source is thus proportional to the vapor pressure and the carrier gas flow.

Equation (4.6) can be used to fit deposition rate data of an OVPD system. Every source of a system has to be calibrated before it is used to determine the deposition rate versus source flow.

Based on (4.6), rQFit, which is a calibration script generator and calibration data fit software, was written during this work and is explained in chapter 10.1.2. An exemplary calibration curve fit is shown in Fig. 4.4.

![Calibration data of NPB and fit based on equation (4.6).](image)

Fig. 4.4: Calibration data of NPB (compare following section 4.3.1) and fit based on equation (4.6).

The fitted data are only useful between the minimum and maximum utilized source flow of 20 and 500 sccm. At low source flows, a linear approximation between deposition rate and source flow can be assumed. However, if a source flow lower than a minimum limit (e.g. 20 sccm) is chosen, the MFC closes completely. The source flow cannot be decreased linearly to 0 sccm.

### 4.3 OLED Production

#### 4.3.1 Overview of Organic Materials

In Tab. 4.1, all organic materials processed within this work are listed with their according HOMO and LUMO energies. HOMO energies are given by the material suppliers and based on cyclovoltammetry (CV) [66] measurements or calculated from UPS [67] measured values via:
LUMO energies are calculated from HOMO energies plus an energy gap. The optical absorption edge determines the energy gap.

\[
E_{\text{LUMO}}^{\text{HOMO}} = 1.01 \text{ eV} + 0.88E_{\text{Evac}}^{\text{HOMO}}
\]

(4.7)

**Tab. 4.1**: Organic materials utilized in this work with according HOMO and LUMO energies referenced to $E_{\text{Evac}}$.

<table>
<thead>
<tr>
<th>material abbreviation</th>
<th>official material name</th>
<th>properties</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq$_3$</td>
<td>tris-(8-hydroxyquinoline) aluminum</td>
<td>fluorescent green emitter</td>
<td>5.4</td>
<td>2.9</td>
</tr>
<tr>
<td>CBP</td>
<td>4,4'-bis(carbazol-9-yl)-biphenyl</td>
<td>bipolar conductor, high-triplet host</td>
<td>5.7</td>
<td>2.1</td>
</tr>
<tr>
<td>CGX150</td>
<td>CGX-150-EL, Ciba, (see Ir(MDQ)$_2$(acac))</td>
<td>phosphorescent red emitter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETM001</td>
<td>Philips OLED material</td>
<td>electron injection material</td>
<td>5.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Ir(MDQ)$_2$(acac)</td>
<td>Ir(III)bis(2-methylidibenzo[f,h]quinoxaline) (acetylacetonate)</td>
<td>phosphorescent red emitter</td>
<td>5.3</td>
<td>2.7</td>
</tr>
<tr>
<td>Ir(piq)$_3$</td>
<td>tris-(1-phenyl-isoquinoline)-Ir</td>
<td>phosphorescent red emitter</td>
<td>4.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Ir(ppy)$_3$</td>
<td>tris-(phenyl-pyridyl)-Ir</td>
<td>phosphorescent green emitter</td>
<td>5.1</td>
<td>2.3</td>
</tr>
<tr>
<td>NDP002</td>
<td>NDP-2, Novaled OLED material</td>
<td>p-dopant</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>NPB</td>
<td>N,N'-diphenyl-N,N'-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine</td>
<td>hole conductor, low-triplet host</td>
<td>5.2</td>
<td>2.4</td>
</tr>
<tr>
<td>SEB115</td>
<td>SEB-115, Merck OLED material</td>
<td>fluorescent blue emitter</td>
<td>5.1</td>
<td>2.3</td>
</tr>
<tr>
<td>SMB013</td>
<td>SMB-013, Merck OLED material</td>
<td>fluorescent blue host</td>
<td>5.7</td>
<td>2.7</td>
</tr>
<tr>
<td>TCTA</td>
<td>4,4',4''-tris(N-carbazolyl)-triphenylamine</td>
<td>hole conductor, high-triplet host</td>
<td>5.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>
4.3.2 Stargate Substrate Design

Due to the complexity of OLED, theoretical knowledge about their functionality is mostly only valid for idealized model systems. When it comes to the processing of organic layer stacks with multiple layers of various functions, the experimental throughput is essential to investigate effects of variations applied to the organic layer stack. The more data available, the easier it is to find generally valid connections. As a consequence, a crucial factor for fast OLED development is the number of experiments per time which can be realized within a certain system.

At the beginning of this work, on one substrate only one organic layer stack could be deposited followed by cathode metallization, encapsulation and measuring. This limited the number of possible organic layer stacks which could be investigated.

The OVPD system available offers a rotation function as well as separated substrate and mask lift mechanics. To increase the possible organic layer stack throughput and to reduce the handling effort, rotation is utilized to deposit independent organic layer stacks during one process run.

The concept of a rotation-symmetric substrate setup is shown in Fig. 4.5.

All devices on a substrate except one are covered by the organic mask. It is crucial that the deposited organic layers do not get in contact with the hot organic mask, so that a spacer mask is introduced as a separating layer. During a rotation step, the organic/spacer mask package is lifted, followed by a rotation of the substrate and lowered again. The deposition can be performed sequentially on the different elements.
of a single substrate. It is not necessary to lift the spacer mask, but the current system setup can only lift the organic and spacer mask concurrently.

After the concept of organic and spacer mask was proven to work successfully, a special research substrate with 8-fold rotation symmetry was designed (Fig. 4.6).

The substrate consists of 8 independent devices each having two light-emitting dots (1 cm² in area each). The distance between the active area and the organic mask edge is set to 1 cm to prevent any kind of edge effect. Edge effects can occur if the mask is not aligned well to the substrate. A disturbed carrier gas flow influences the thickness of the organic layers in the surrounding of the mask edge. If the thickness of the organic layers is not constant versus the whole active area, shifts in color coordinates or luminance can be observed.

For comparison, an identical organic layer stack is deposited sequentially on each of the 8 devices and measured. The measurement is shown in Fig. 4.7.
The current efficacy (21.9±0.9 cd/A) as well as the color coordinates of all devices are highly reproducible. Rotation-symmetric Stargate substrates are used for OLED development.

4.3.3 Manufacturing Process and Equipment

ITO-coated (150 nm) glass substrates are cleaned in an automated system by mechanically scrubbing under de-ionized water and drying in an inert N₂ atmosphere. Before processing, substrates are either activated in a plasma barrel reactor at 400 W for 5 min at 1 mbar O₂ partial pressure or in a UV/ozone cleaner under atmospheric conditions.

For R&D purposes, a cluster production system from AIXTRON (Gen1) is available in a clean-room environment. Substrate sizes up to 215x15 cm² can be coated by this equipment. In Fig. 4.8, a photo of the system including the organic material source cabinet, deposition chamber, handler chamber and glovebox is shown.
4. Production Techniques and Equipment

Additional information and investigations about different organic material sources can be found in the appendix (chapter 10.2). In Fig. 4.9, the setup is schematically drawn.

![Fig. 4.8: AIXTRON Gen1 system.](image_1)

**Fig. 4.8:** AIXTRON Gen1 system.

**Fig. 4.9:** Top-view of OVPD setup with deposition chamber, handler chamber, HV metallization and glovebox.

After substrate activation, the substrates are transferred into an \( N_2 \)-purged glovebox and from there on via the handler chamber to the OVPD deposition chamber. The deposition of the organic materials is fully controlled by software scripts. The introduction of Stargate substrates increased the possible number of organic layer
stacks significantly, so that the manual script writing had to be accelerated. During this work, RGen software (compare chapter 10.1.3) was written. RGen automatically creates a machine-readable script out of a given organic layer stack design applying the most recent calibration data (from rQFit software).

After depositing the organic layers, the glass substrates are transferred through the handler chamber at 0.9 mbar N₂ atmosphere to the HV chamber. The base pressure of the HV chamber is below 10⁻⁶ mbar. An automatic Al feed mechanism supplies Al pins to an evaporation boat, so that the HV chamber has to be opened only very infrequently to refill Al pins. Beside the Al evaporation, two additional crucibles are installed in the chamber. One of them is used to evaporate LiF (0.5 nm) prior to Al cathode (100 nm) deposition. The other is used to evaporate WO₃ or MoO₃.

As described in chapter 3.2.5, OLED can be qualified in-situ in the glovebox by a spectrometer before encapsulation. But if necessary, without a break of the N₂ atmosphere, an encapsulation in a different glovebox is possible in a later step.
5 Study of Interface Stabilization

In this chapter, different concepts to realize homogeneous and long-term stable hole injection (even at elevated temperatures) from ITO to first organic layer are investigated and compared. Concurrently, p-doping in an OVPD system is improved and for the first-time, a single run p-doped OVPD OLED is presented.

5.1 Inhomogeneous Active Area

ITO/organic interface properties and effects are crucial for charge injection into OLED (compare chapter 3.3). Therefore, stable interface properties versus operating time are important for OLED lifetime and homogenous luminance over the active area. It is found that by operation time or if devices are stored at elevated temperatures, inhomogeneities in luminance appear on the active area (Fig. 5.1).

![Fig. 5.1](image)

**Fig. 5.1:** Photo of inhomogeneous active area (on-state) of OLED (3.8 cm x 3 cm) after storage at elevated temperatures. 4.25 h at 70°C (left). 21 h at 80°C (right).

In Fig. 5.2, the organic layer stack of the investigated OLED of Fig. 5.1 is shown.

![Fig. 5.2](image)

**Fig. 5.2:** Organic layer stack of investigated OLED.
A 150 nm HTL consisting of NPB is followed by a 30 nm fluorescent blue EL and a 20 nm ETL consisting of ETM001. The blue EL consists of the host material SMB013 doped with 5% vol. of the fluorescent blue emitter SEB115 (for organic materials compare Tab. 4.1). At 1000 cd/m², a current efficacy of 7.7 cd/A at a drive voltage of 3.7 V can be measured. The appearance of inhomogeneities over the active area is a result of unstable hole injection at the ITO to HTL interface. If the hole injection is enhanced for example by a dipole layer, the partial degradation of this dipole layer causes inhomogeneous emission (Fig. 5.3).  

**Fig. 5.3:** Closed dipole layer and homogeneous hole injection and emission over active area (left) and degraded dipole layer followed by inhomogeneous emission (right).

To operate OLED at higher luminance (and thereby higher temperatures if not cooled) or for storage in rough environments with large temperature variations like cars, a more stable interface has to be developed. Different processes are commonly applied to activate the ITO surface after particle cleaning and removal of gross contaminants. While the usage of oxygen and an O₂ plasma or UV/Ozone treatment is an often utilized method to create a surface dipole on the ITO surface, different alternative concepts exist as well. As explained in chapter 3.3, the injection can be enhanced by three different methods, which are:

- dipole layers
- band-bending by doping
- charge extraction layers

All of these approaches are investigated in the following. Compared to an O₂ plasma, the creation of a more stable dipole layer is realized by connecting functionalized molecules to the ITO surface via wet chemistry (chapter 5.2). Stabilization by band-bending is investigated by p-doping the HTL at the interface (chapter 5.3) and the stable extraction of charge carriers of the first organic layer is investigated employing thin oxide buffer layers (chapter 5.4).
To evaluate the different approaches in terms of interface stability between ITO and first organic layer, large-area (e.g. 3.8 cm x 3 cm) OLED (organic layer stack shown in Fig. 5.2) are stored at elevated temperatures of 70°C in the off-state, which simulates the storage in a rough environment. However, 70°C guarantees to be lower than the glass transition temperature of NPB of 95°C [47] (lowest glass transition temperature of investigated OLED stack). An energetically long-term stable interface should not be affected by the storage. To measure the quality of the interface, the active area is checked periodically for inhomogeneities in the on-state. Although the optical inspection of inhomogeneities is to some extent depending on how good the person who inspects the OLED is trained, it is the only feasible method to acquire information about the interface. In this way, macroscopic result of microscopic effects at the ITO/organic interface is observed. It is probably not possible to investigate the effect on a microscopic scale. Necessary would be a microscopic method which could detect electronic changes at the interface. In principle, electron loss spectroscopy (EELS), which belongs to the group of transmission electron microscopy (TEM), would be suitable. But with regard to the electron exposure density necessary for high resolution (0.1 to 0.2 C/cm²/s), a critical electron dose for organic materials of $10^{-3}$ C/cm² [68] would be reached within seconds. If electrons are excited in an organic molecule, the relaxation can easily destroy bonds (radiolysis), which was observed already in very early TEM investigations [69-70]. Apart from the visual description of inhomogeneities, a further quantitative qualification of the interface is only possible in some special cases. The lifetime e.g. is sensitive to many different factors (compare chapter 3.5 and chapter 7), so that a direct connection between the stability of the interface and the lifetime is mostly not given. Furthermore, if Fermi energy pinning occurs at the ITO/organic interface, IV curves do not necessarily change if different methods of activation are applied.

As described in chapter 4.3, O₂ plasma cleaning is the standard activation procedure in this work. A comprehensive overview of O₂ plasma cleaning of ITO surfaces is given in [71]. An increase in the work function after O₂ plasma treatment can be traced back to the creation of a surface dipole. It was found that the work function increase has a positive influence on the injection of holes from the ITO into the HOMO of the adjacent organic layer. But even if O₂ plasma activation guarantees excellent short-term injection properties, it does not seem to be the ideal method to guarantee a long-term stable ITO/organic interface. At elevated storage temperatures of 70°C, inhomogeneities in the active area of OLED appear after 240 h. The excellent short-term injection properties of O₂ plasma activated substrates are not influenced if the substrates are stored in N₂ atmosphere (at 25°C and up to 24 h) before the deposition of organic layers.
5.2 Stable Dipole Layer by Phosphonic acid

Alternatively, a dipole layer can be created via the wet-chemical attachment of functionalized molecules to the ITO surface. Suitable molecules have to be able to form a chemical bond to the ITO surface while at the same time have to have a negatively polarized part pointing away from the surface (Fig. 3.10 (A) and Fig. 5.4).

![Diagram showing energy levels and work function](image)

**Fig. 5.4:** Unmodified ITO/organic interface (left). ITO surface dipole shifts $E_{\text{vac}}$ and lowers the hole injection barrier $E_{\text{barrier}}$ (right).

The ITO surface dipole which is shown in Fig. 5.4 (right) raises the vacuum level $E_{\text{vac}}$ and enhances the injection of holes into the HOMO of the organic material. The potential energy of holes crossing the surface dipole is lowered by the amount of the dipole energy $\Delta E_{\text{dipole}}$.

Possible molecules to realize a surface dipole belong to the group of silanes, carboxylic acids and phosphonic acids [34], while phosphonic acids show the strongest bond to ITO surface. The attachment of different phosphonic acids with functionalized side groups to the ITO surface is described in [72]. Compared to air plasma activated OLED, a comparable efficiency could only be found if functionalized groups creating an ITO surface dipole which increases the work function of the ITO were chosen. In [73], additional functionalized phosphonic acids were investigated in terms of altering the ITO work function and OLED efficiency. Depending on the functional side group, the work function of ITO could be modified between 4.4 eV and 5.4 eV. In [74], the hole injection barrier of phosphonic acid treated ITO surfaces (work function between 4.9 eV and 5.4 eV) to NPB is investigated. Due to Fermi level pinning at the interface (work function of ITO pinned to HOMO energy of NPB), no influence on the hole injection barrier was found (injection barrier in all cases 1 eV). If the work function of the substrate is lower than the HOMO energy of the organic material, the injection barrier generally decreases with increasing work function of the substrate (e.g. unmodified to phosphonic acid treated ITO). However, as soon as the work function
comes close (in the range of 1 eV) to the HOMO energy of the organic material, the injection barrier does not seem to decrease any longer but remains constant [74]. Consequently, the work function of unmodified ITO has to be increased to guarantee a low hole injection barrier, but it is not necessary to match exactly the HOMO energy of the following organic material. Additionally to the work function, the surface energy of ITO is altered due to the attachment of phosphonic acids. A hydrophilic surface can be found after an $O_2$ or air plasma activation, while a phosphonic acid activation creates a hydrophobic surface [73].

Commercially available, pentafluoroethylphosphonic acid (here: FEPA) (Fig. 5.5) is chosen in this work to activate the ITO surface. Due to the difference in electronegativity FEPA molecules have a dipole moment.

The activation of ITO for OLED by this kind of functionalized phosphonic acid was never reported before. The complete activation procedure is shown in Fig. 5.6 schematically.

For ITO activation, a 1 mM solution of FEPA in chloroform and ethanol (2:1 ratio) is prepared and the ITO substrates are stored for 24 h in the solution. To complete the bonding between the phosphonic acid and the ITO substrate, the substrate is stored for 1 h on a heat plate at 140°C. In a next step, the substrate is cleaned from unbound molecules in an ultrasonic ethanol bath. After the activation procedure, a blue OLED according to the organic layer stack of Fig. 5.2 is deposited on the substrate. At 1000 cd/m², a current efficacy of 7.8 cd/A and 3.9 V drive voltage can be measured. This is comparable to the $O_2$ plasma activated reference device. In terms of drive voltage, it is further investigated if the activation by an $O_2$ plasma or FEPA results in different IV characteristics. In Fig. 5.7 (left), the IV curves of OLED with both activation methods are plotted. No significant difference in the IV curves can be found.
To investigate the long-term stability of the phosphonic acid activation method, the processed large-area (and FEPA activated) OLED are stored for 641 h at 70°C. No inhomogeneity can be found in the active area, so that the activation of the ITO surface by FEPA is a possibility to realize a long-term stable interface. In contrast, the commonly utilized oxygen-based dipole layer is not long-term stable and causes inhomogeneities (Fig. 5.1). It can be concluded, that a stable FEPA dipole layer was created and is present on the ITO surface (Fig. 5.7 (right)).

However, one major problem of the activation procedure described before seems to be the left-over of residuals of the solvents on the substrate. This can result in some artifacts in the active area of the OLED. Even though the activation by FEPA is suitable to create a long-term stable dipole layer on the ITO surface, an ITO stabilization procedure which could be directly integrated into a HV or OVPD process would be favorable compared to a wet-chemical approach. This would also circumvent the problem of inhomogeneities caused by the evaporation residua of the solvents.

5.3 p-Doping in an OVPD System

Before the properties and long-term stability of an ITO to p-doped organic layer interface can be investigated as an alternative and vacuum based process, p-doping in an OVPD system itself has to be improved. The first experiments investigating p-doping of organic semiconductors in an OVPD system were conducted in [37]. NPB was doped by NDP002 (compare with organic material list in Tab. 4.1) utilizing the same OVPD system as in this work. It was found that it is in principle possible to p-dope NPB, but several limitations remained. It became obvious that the p-dopant NDP002 behaves differently compared to other organic materials. After opening the source
valve, the maximum deposition rate of NDP002 was reached with a delay of 1900 s (start-up effect), while after closing the source valve, a significant NDP002 rate could still be measured for at least 5 h (follow-up effect). The follow-up deposition rate of NDP002 prevents the processing of a complete OLED with a p-doped hole injection layer (HIL) in one step. Due to its low triplet energy, NDP002 would quench the emission completely if small amounts are incorporated in the EL of an OLED.

A p-dopant is a strong oxidizing agent (LUMO energy qualitatively shown in Fig. 3.9). One possible source of the delayed NDP002 deposition might therefore be the p-dopant, which adsorbs to the Al showerhead. Only after the adsorption and desorption of NDP002 molecules to and from the showerhead surface has reached equilibrium, the maximum deposition rate of NDP002 can be measured. After the source valve is closed, the desorption of NDP002 molecules from the showerhead surface can account for a significant follow-up deposition rate of NDP002. A second possible source of the NDP002 contamination of the following organic layers might be the diffusion of previously deposited (in direct proximity to the substrate) NDP002 molecules towards the substrate.

To prevent delayed NDP002 deposition, the Al showerhead is replaced by a version manufactured out of a more inert material (stainless steel). All runlines are already manufactured out of stainless steel. To prevent the diffusion of previously deposited NDP002 molecules, the deposition chamber in the surrounding of the substrate is cooled below the evaporation temperature of the organic materials (diffusion barrier). In the following, it is investigated if the diffusion barrier has an influence on the p-doping utilizing the standard Al showerhead and, how the upgrade to a stainless steel showerhead influences the p-doping.

5.3.1 p-Doping with Diffusion Barrier (but Al Showerhead)

A cooled (20°C) diffusion barrier is installed close to the substrate (Fig. 5.8). The cooled diffusion barrier is integrated to prevent that previously deposited organic materials with relatively low evaporation temperatures (like NDP002) diffuse towards the substrate and into the next organic layer.
The p-dopant NDP002 is investigated. To demonstrate successful p-doping, hole-only devices consisting of 300 nm NPB are processed according to Fig. 5.9 (left). In the case of device 2 and 3, a doping concentration of 10% is aspired. A realistic assumption is made for the deposition rate of NDP002 taking the source temperature and given data from former experiments at AIXTRON. The exact deposition rate of the p-dopant is not relevant for evaluation. In the case of successful p-doping, the hole conductivity should increase by several orders of magnitude with high tolerance regarding the doping concentration.

Fig. 5.8: Cooled diffusion barrier prevents the diffusion of previously deposited organic materials in the following organic layers.

![Fig. 5.8: Cooled diffusion barrier prevents the diffusion of previously deposited organic materials in the following organic layers.](image)

Fig. 5.9: Hole-only devices consisting of NPB and NPB doped with NDP002 (left). Current density versus voltage for the hole-only devices (right).

![Fig. 5.9: Hole-only devices consisting of NPB and NPB doped with NDP002 (left). Current density versus voltage for the hole-only devices (right).](image)
In Fig. 5.9 (right), the current density versus voltage for the hole-only devices of Fig. 5.9 (left) is shown. The curve progression of device 1 is the one of a typical undoped NPB layer. Up to a voltage of 2 V, the current is injection-limited, while above, a transition to a SCLC can be seen. The SCLC mobility is field-dependent and therefore, the slope changes with increasing voltage. Further information can be found in [8, 18]. The curve progression of device 2 describes a p-doped NPB layer. The curve progression is symmetric because the doping allows holes to be injected at the cathode side of the device as well (Fig. 5.10).

Compared to the undoped device 1, the current density at the same voltage increases by 3-4 orders of magnitude in Fig. 5.9 (right). The equilibrium deposition concentration of NDP002 does not seem to be reached in device 2, so that device 3 shows an even higher current density with voltage. Intentionally, only NPB is deposited in device 4. Nevertheless, due to a follow-up deposition of NDP002, small amounts of it seem to be doped into the NPB layer, so that the current density versus voltage is higher than the one of device 1. The curve progression of device 4 is anti-symmetric and consequently, at the cathode side of the NPB layer, the NDP002 concentration must be low again, so that the injection of holes is no longer possible.

To more accurately determine the follow-up deposition rate, after the deposition of p-doped NPB layers followed by an increasing waiting time, monochrome red OLED (without any intentional p-doping) are processed. The organic layer stack of the red reference OLED is explained in detail in chapter 6.2. Commonly, 31 cd/A can be measured at a drive voltage of 3.3 V at 1000 cd/m². At the same luminance, the current efficacy and drive voltage of the processed red OLED with increasing waiting time are shown in Fig. 5.11.
Immediately following the deposition of NDP002, the concentration of the p-dopant seems to be high enough to quench the emission in the EL of the red OLED completely. The current efficacy is below 5 cd/A and the voltage above 6 V. Between 4 and 7 h later, the current efficacy reaches its normal value of more than 30 cd/A again, whereas the voltage after 13 h has not yet reached its normal value of 3.3 V, but remains higher (3.7 V). This follow-up deposition rate of NDP002 is comparable to the results in [37]. In conclusion, the cooled diffusion barrier does not seem to influence the follow-up deposition rate of the NDP002 p-dopant.

In addition to the adsorption of the p-dopant to the Al showerhead, gas phase reactions of the p-dopant on collision with other molecules on the way through the runlines and mixing unit should be taken into account. An NDP002 molecule in contact with e.g. NPB in the gas phase can react and form a complex. If these complexes hit the heated walls of the system, they might at least partially stick to them due to their higher mass (Fig. 5.12).
To investigate this possibility, a constant source flow of TMM004 is chosen and a layer thickness of 100 nm is deposited on a silicon wafer. TMM004 instead of NPB is chosen because it is an electron conductor and has a very low HOMO energy. The LUMO energy of NDP002 is not known, but the reaction probability should be minimized. In the following, a defined source flow of NDP002 is added to the TMM004 source flow. The total organic layer thicknesses deposited on the silicon wafer are shown in Fig. 5.13.

![Fig. 5.13: Thickness of TMM004 and TMM004+NDP002 on silicon wafer.](image)

The expected TMM004 layer thickness of 100 nm is reached if only the TMM004 source valve is opened. If additionally, the source valve of NDP002 is opened, the organic layer thickness should at least not decrease. But, this is the case. The higher the source flow through the opened NDP002 source (either 500 or 100 sccm), the higher the reduction of the deposited total organic layer thickness. This can only happen if parts of the TMM004 are deposited somewhere on the way to the substrate. A reaction between TMM004 and NDP002 has to be taken into account. It is therefore questionable if gas phase p-doping without any start- and follow-up deposition rate is possible even if inert materials are utilized for the equipment. On the other hand, if compared to a VTE system, the long interaction pathway in the gas phase of an OVPD system increases the efficiency of p-doping and the concentration of the p-dopant could be decreased, this would be positive in terms of manufacturing costs.

### 5.3.2 p-Doping in an All Stainless Steel OVPD System

In the framework of a system upgrade, the Al showerhead of the OVPD deposition chamber is replaced by a version manufactured out of stainless steel. In contrast to Al, stainless steel is assumed to be more inert against oxidation by a p-dopant, so that it should be possible to decrease the start-up and follow-up deposition rate of the p-
dopant in an all stainless steel OVPD system. Again, to investigate the successful p-doping, hole-only devices consisting of NPB are processed (Fig. 5.14 (left)). A p-dopant (NDP002) concentration of 10% is aspired. In Fig. 5.14 (right), the current density versus voltage is plotted for different hole-only devices consisting of 150 nm NPB.

![Device 1+3+4](image)

![Device 2](image)

**Fig. 5.14**: Hole-only devices consisting of NPB and NPB doped with NDP002 (left). Current density versus voltage for the hole-only devices (right).

Device 1 in Fig. 5.14 (right) is processed before the p-dopant source valve was opened and shows the typical curve progression of an undoped NPB organic layer. Device 2 shows the curve progression of a NDP002 doped NPB organic layer. As expected, the current density increases by 3-4 orders of magnitude at the same voltage and a symmetric behavior can be measured. Device 3 and device 4 are processed with the NDP002 source valve closed again. Device 3 is processed directly after a p-doped NPB layer is deposited, while device 4 is deposited 6 h later. Both devices show a higher current density compared to device 1 and no change after 6 h occurs. A follow-up deposition rate of NDP002 can be assumed. However, the doping concentration is too low to allow the injection of holes from the Al electrode of the hole-only devices.

To investigate the follow-up deposition rate of NDP002, monochrome red OLED with a p-doped HIL according to Fig. 5.15 are processed (further information about the basic (non p-doped) organic layer stack can be found in chapter 6.2). Between the p-doped and undoped part of the organic layer stack, a process break is inserted. During the process break the substrate stays in the deposition chamber.
In Fig. 5.16, the IV curve of a red reference OLED without a p-doped HIL, as well as two red OLED with p-doped HIL and a process break of 0 and 10 min between the p-doped and undoped part are shown.

The current density of the OLED with p-doped HIL is lower compared to the reference OLED. If a small fraction of NDP002 is incorporated into the EL or ETL, it can act as trap states reducing the conductivity and increasing the necessary drive voltage. Concurrently, due to its low triplet level, NDP002 acts as emission quencher in the EL. However, with increasing process break time between the p-doped and undoped part of the organic layer stack, the IV curve shifts to higher values again and comes in close vicinity to the IV curve of the reference device. Fig. 5.16 clarifies that even in an all stainless steel OVPD system, a follow-up deposition rate is present. Does this follow-up deposition rate still quench the emission significantly? In Fig. 5.17 (left), the evolution of the current efficacy and drive voltage of OLED with different process break times are shown (organic layer stack according to Fig. 5.15). Without a process break, the current efficacy decreases to 69% of the reference OLED. This is already a strong
improvement compared to the investigations with an Al showerhead (a decrease in current efficacy to 7% of the reference OLED was measured). If a 10 min process break is inserted between p-doped and undoped layer, the current efficacy has nearly reached the value of the reference OLED.

![Graph showing current efficacy and voltage of p-doped red OLED with different time of process break between doped and undoped hole-injection layer](image)

**Fig. 5.17:** Current efficacy and voltage of p-doped red OLED with different time of process break between doped and undoped hole-injection layer (left). Comparison of the Al and stainless steel showerhead (right).

However, a slightly higher drive voltage of 3.5 V remains compared to the reference OLED (3.3 V). Between 10 to 60 min process break time, the drive voltage decreases to 3.4 V, which can be regarded as the reference OLED drive voltage. Fig. 5.17 (right) visualizes the difference (of current efficacy versus process break time) between the Al and stainless steel showerhead impressively.

In conclusion, p-doping in an all stainless steel OVPD system reduces the follow-up deposition rate of the p-dopant dramatically. A slight follow-up deposition rate can still be observed in the IV curves of hole-only devices as well as in complete OLED. This might be due to gas phase reactions and complexes adsorbed and released by e.g. runline walls. The insertion of a process break time of 10 min, in which the substrate can stay in the deposition chamber, is enough to reduce the follow-up deposition rate significantly. p-Doped OLED which are comparable in current efficacy and drive voltage to undoped OLED can be processed. Note that the p-doping does not show any positive effect on the OLED performance compared to undoped devices. This is reasonable because an O₂ plasma treated ITO substrate already does not have a relevant injection barrier to the hole-transporting NPB layer. Furthermore, the influence of p-doping is relatively low in the case when OLED having only thin HTL with a good conductivity (like NPB) at moderate current densities are investigated.
Even if the p-doping can be controlled in an all stainless steel OVPD system, the following questions should be answered in future:

- Does the p-dopant react in the gas phase with the host? Is this kind of doping more effective compared to conventional p-doping in a VTE system? Does the reaction complex between dopant and host have a higher evaporation temperature?
- Can a possible reaction of the p-dopant and the system walls be further suppressed if more inert materials than stainless steel are utilized?
- Are there any alternatives to organic and temperature-sensitive (and expensive) p-dopants which can be processed specifically in an OVPD system?

### 5.3.3 p-Doped Interface

After successful p-doping, the option to stabilize the ITO/organic interface by doping (compare chapter 3.3) is investigated. The organic layer stack of the investigated blue OLED is shown in Fig. 5.18.

![Organic layer stack of blue OLED investigating the stability of an ITO to p-doped NPB layer interface.](image)

The organic layer stack is comparable to the one of Fig. 5.2, but with some part of the NPB layer doped with NDP002. Large-area OLED (3.8 cm x 3 cm) with different thicknesses of the p-doped NPB layer followed by an undoped NPB layer are processed and stored at 70°C. Even if no positive effect on the OLED efficiency and drive voltage could be observed in the previous chapter, the ITO/organic interface can be long-term stabilized by p-doping (Tab. 5.1).

### Tab. 5.1: p-Doped monochrome blue OLED stored at 70°C.

<table>
<thead>
<tr>
<th>p-doped layer thickness [nm]</th>
<th>time stored at 70°C [h]</th>
<th>homogeneity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>inhomogeneous</td>
</tr>
<tr>
<td>5</td>
<td>1500</td>
<td>slightly inhomogeneous</td>
</tr>
<tr>
<td>10</td>
<td>2500</td>
<td>no inhomogeneity</td>
</tr>
</tbody>
</table>
To realize an effective Fermi level pinning and long-term stable hole-injection from the ITO into the NPB layer, a certain minimum thickness (at least 10 nm) of the NPB has to be p-doped.

To verify the stabilization effect, the p-doped and undoped NPB layer are switched in order. Directly at the ITO interface, 10 nm of undoped NPB are deposited followed by 140 nm of p-doped NPB (and another 10 nm of undoped NPB as spacer layer). As expected, the devices become inhomogeneous if stored at 70°C.

Due to the easy process integration, the p-doping of the HIL at the ITO interface is the preferred option for stabilization compared to FEPA.

5.4 Oxide Buffer Layers for Electron Extraction

In [35-36], molybdenum oxide (MoO₃) was investigated as an oxide buffer layer situated between the ITO and the first organic layer. The oxide layer is able to enhance the injection of holes. Via the CB of MoO₃ (electron affinity of 6.7 eV) electrons are extracted from the HOMO (ionization energy of 5.4 eV) of the first organic layer (NPB) and transported to the ITO anode (Fig. 3.10 (C)). Due to electron transfer from the NPB HOMO to the CB of MoO₃, a dipole layer of 2.1 eV is present [36] at the MoO₃/NPB interface. This dipole layer and the concurrent shift of the vacuum level results in a low (0.6 eV [36]) energetic barrier for holes crossing the NPB/MoO₃ interface.

It should be possible to stabilize the ITO/organic interface by an oxide buffer layer and guarantee a stable hole injection (chapter 3.3). The same mechanism should work for tungsten oxide (WO₃) having a comparable energetic structure, so that both oxides are investigated in terms of interface stabilization in the following. The electronic properties and conductivity of transition metal oxides like MoO₃ and WO₃ is strongly dependent on the exact stoichiometry, while non-stoichiometric oxides are n-type semiconducting [75-76].

To investigate MoO₃, monochrome OLED with and without oxide buffer layer are processed and qualified at 1000 cd/m² (Tab. 5.2). The organic layer stack of the monochrome blue (SEB115) OLED can be found in chapter 5.1, but is explained in detail in chapter 6.2 along with the organic layer stacks of the monochrome red (CGX150) and green (Ir(ppy)₃) OLED. The complete organic layer stack of the white OLED is presented in chapter 8.2. In theory, one closed monolayer of MoO₃ should be suitable to alter the injection properties of the ITO surface. A 3 nm layer of MoO₃ (fully oxidized) is evaporated on the substrate. This guarantees a closed layer without an increase in drive voltage.
5. Study of Interface Stabilization

**Tab. 5.2:** Current efficacy and voltage of OLED processed without and with MoO$_3$ buffer layer at 1000 cd/m$^2$.

<table>
<thead>
<tr>
<th>emitter</th>
<th>0 nm MoO$_3$</th>
<th>3 nm MoO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta_c$ [cd/A]</td>
<td>U [V]</td>
</tr>
<tr>
<td>CGX150</td>
<td>28.2</td>
<td>2.9</td>
</tr>
<tr>
<td>Ir(ppy)$_3$</td>
<td>43.0</td>
<td>3.1</td>
</tr>
</tbody>
</table>

According to Tab. 5.2, MoO$_3$ does not have a significant influence on the current efficacy and drive voltage of the OLED. Next, large-area OLED are processed with an oxide buffer layer and stored at 70°C. Even after 2000 h of storage, no inhomogeneities in the active area can be observed. Therefore, MoO$_3$ can be applied to stabilize ITO/organic interfaces.

The same investigations are conducted with WO$_3$, while the oxide buffer layer thickness is reduced to 1 nm.

**Tab. 5.3:** Current efficacy and voltage of OLED processed without and with WO$_3$ buffer layer at 1000 cd/m$^2$.

<table>
<thead>
<tr>
<th>emitter</th>
<th>0 nm WO$_3$</th>
<th>1 nm WO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta_c$ [cd/A]</td>
<td>U [V]</td>
</tr>
<tr>
<td>CGX150</td>
<td>28.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Ir(ppy)$_3$</td>
<td>48.5</td>
<td>3.2</td>
</tr>
<tr>
<td>SEB115</td>
<td>8.8</td>
<td>3.9</td>
</tr>
<tr>
<td>white</td>
<td>24.2</td>
<td>3.9</td>
</tr>
</tbody>
</table>

According to Tab. 5.3, WO$_3$ does not have a significant influence on the current efficacy or drive voltage, either. Large-area OLED with a WO$_3$ buffer layer do not show any inhomogeneities in the active area after 1500 h of storage at 70°C.

In summary, MoO$_3$ as well as WO$_3$ are suitable to stabilize the ITO surface.

### 5.5 Overview of Stabilization Concepts

Tab. 5.4 gives an overview of the different stabilization concepts applied to the ITO surface and the interface stability time of devices stored at 70°C. Specifically the stabilization by transition metal oxides (MoO$_3$, WO$_3$) seems to be extraordinary long-term stable (p-doped devices show inhomogeneities if the p-doped HTL is too thin). In
no case inhomogeneities appeared and it can be concluded that the interface is stable even several thousand hours.

**Tab. 5.4: Overview of stabilization methods.**

<table>
<thead>
<tr>
<th>stabilization concept</th>
<th>interface stability if stored at 70°C [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ plasma</td>
<td>&lt;240</td>
</tr>
<tr>
<td>phosphonic acid (FEPA)</td>
<td>&gt;641</td>
</tr>
<tr>
<td>p-doping</td>
<td>&gt;2500</td>
</tr>
<tr>
<td>MoO₃</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>WO₃</td>
<td>&gt;1500</td>
</tr>
</tbody>
</table>

Different mechanisms (compare chapter 3.3) can be utilized to realize nearly barrier-free hole injection from ITO to first organic layer. Concepts applying these mechanisms were presented and compared in terms of long-term interface stability even at elevated temperatures. Depending on the application, the concepts are more or less suitable. If only the initial photometric values (like efficiency) are of importance and the injection properties do not need to be long-term stable at elevated temperatures, O₂ plasma activation is an easy and fast option. ITO substrates can be activated before processing and independent of the deposition tool. If p-doped HIL can be deposited easily and without limitation (like in VTE tools), interface stabilization by p-doping can be the choice. Fully integrated into the organic deposition process, a long-term stable injection can be realized without much effort. Due to the activation procedure (very clean wet-chemical process necessary), the application of phosphonic acids can be taken into account if substrates have to be activated on an industrial scale. If long-term stable interfaces in small numbers are needed (specifically for OVPD), the deposition of transition metal oxides is the recommended option. In future, organic materials having comparable energetic properties to transition metal oxides should be investigated (e.g. 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HAT-CN)).
6 Cross-faded Emission Layer

In this chapter, different emission layer (EL) concepts are investigated and compared employing monochrome as well as two-emitter yellow OLED. The required and desired properties of EL are discussed and it is investigated how OVPD can help to improve the EL. The design of the EL is crucial for high efficiency and lifetime.

6.1 Mixed-host and Cross-faded Emission Layer

Different concepts to realize an EL exist (compare chapter 3.4) and in most cases, the mixture of two materials (emitter and host) is the preferred choice. To some point, this is a result of the widely available VTE tools. With an increasing number of materials to mix, VTE deposition of organic layers becomes increasingly difficult. An OVPD tool instead offers the possibility to mix materials without limitation (chapter 4.2 and 4.3). The process complexity does not increase with an increasing number of mixed materials. Therefore, different concepts which are advantageous for the design of an EL can be realized.

An EL should have the following properties:

- Laterally broad recombination zone (less emitter degradation, triplet density low).
- Little non-radiative recombination on host molecules.
- Recombination zone restricted to the EL (avoids quenching).
- Recombination zone stable against process variations, different device temperatures and operating points.
- Recombination zone stable against HTL/ETL variations for optical tuning.
- Mobility for both types of charge carriers controllable to influence charge carrier distribution.
- Low energy loss when charge carriers are trapped on emitters.
- High-triplet energies of hosts according to utilized emitters.

With regard to OLED history, an impressive efficiency enhancement was realized when not only a single material was utilized for charge injection, transport and emission, but different functionalized materials were serially deposited [77]. Today, many very
specialized organic materials are available for either charge carrier injection, electron transport, hole transport or emission. It can be concluded that it is advantageous to mix at least three different materials in an EL, namely hole conductor, electron conductor and emitter.

6.1.1 Advantages of Mixed-host Emission Layer

The mixture of one hole- and one electron-conducting host material in an EL was investigated in e.g. [38-40]. Several advantages can be realized by mixing two host materials.

First, the gap between the hole-conducting HOMO and the electron-conducting LUMO can be formed out of two independent materials (compare chapter 3.4 and Fig. 6.1 (left)). In consequence, it would be possible to create a HOMO-LUMO gap in which the HOMO/LUMO of a phosphorescent emitter fits in quite well and no unnecessary energy loss occurs when charge carriers are trapped on emitter molecules.

Second, it is easier to create a HOMO-LUMO gap which is suitable for high-triplet energy emitters. To avoid triplet quenching on host molecules in the case of a high-triplet energy emitter, the host materials have to have higher triplet energies resulting in an even higher HOMO-LUMO gap (Fig. 6.1 (right)). With increasing triplet energy of the emitter, it becomes difficult to find host materials with suitable higher triplet energies and specifically, a HOMO-LUMO gap which fits to the HOMO/LUMO of the emitter. The separation into two host materials (and the possibility to choose the HOMO and LUMO from different host materials) circumvents this problem.

Furthermore, the utilization of different host materials as hole and electron conductor offers the option to choose optimized host materials having high mobilities. In this case, holes and electrons are conducted on different kinds of molecules and the probability of unwanted recombination should be significantly lower as well.
From here on, the host resulting from the combination of the HOMO of the hole-conducting host material and the LUMO of the electron-conducting host material is termed *virtual host*.

The lower drive voltage of a mixed-host EL versus an EL employing a single bipolar host material is shown in Fig. 6.2 (right) and Fig. 6.3 (right).

![Diagram of organic layer stacks](image)

**Fig. 6.2:** Organic layer stacks of different (mixed-host (top) and bipolar host (bottom)) red (TER031) OLED (left) and luminance versus voltage of these devices (right).

In Fig. 6.2 (left), the organic layer stacks of two red (TER031) emitting OLED are shown. The EL of the top OLED consists of a mixture of NPB:TMM004 (mixed-host) and TER031 while the other consists of a mixture of CBP (bipolar host) and TER031. The luminance versus drive voltage for both OLED is plotted in Fig. 6.2 (right).

The HOMO-LUMO gap of CBP is 3.6 eV, while the HOMO-LUMO gap of the virtual host material NPB:TMM004 is 2.6 eV. The luminance onset (set to 50 cd/m²) can be observed at 3.5 V (CBP) and 2.4 V (NPB:TMM004). The luminance onset correlates with the HOMO-LUMO gap and is even lower than the voltage corresponding to the calculated gap. This is possible because the HOMO and LUMO energies are not discrete as assumed for calculation but broadened.

In Fig. 6.3 (left), the organic layer stacks of two green (Ir(ppy)₃) emitting OLED are shown. The EL of the top OLED consists of a mixture of TCTA:TMM004 (mixed-host) and Ir(ppy)₃ while the EL of the bottom OLED is formed out of two emitter-doped organic layers. The first organic layer consists of a CBP:Ir(ppy)₃ mixture and the second consists of a TMM004:Ir(ppy)₃ mixture. Therefore, the bottom OLED is termed double EL OLED. The concept of a double EL was introduced in [37]. The luminance versus drive voltage for both OLED is plotted in Fig. 6.3 (right).
6. Cross-faded Emission Layer

![Organic layer stacks of different (mixed-host (top) and double EL (bottom)) green (Ir(ppy)₃) OLED (left) and luminance versus voltage of these devices (right).](image)

At the luminance onset (set again to 50 cd/m²), the green OLED show a voltage of 2.5 V (TCTA:TMM004:Ir(ppy)₃) and 3.0 V (CBP:Ir(ppy)₃|TMM004:Ir(ppy)₃). The HOMO-LUMO gap of the mixed-host (TCTA:TMM004) OLED can be calculated to 2.7 eV and matches the measured value. The voltage of the double EL OLED cannot be explained by the HOMO-LUMO gap of the employed host materials CBP and TMM004 of 3.6 eV and 3.3 eV. Rather, it can be assumed that the emission takes place at the CBP to TMM004 interface. The HOMO of CBP and the LUMO of TMM004 form a virtual gap for the emitter. This virtual gap can be calculated to 3.1 eV and matches the measured value. The green double EL OLED reveals that the concept of a virtual HOMO/LUMO host is not only valid for completely mixed-host EL, but can work at interfaces, too. Nevertheless, a double EL is a very special design unsuitable for more complex organic layer stacks. Moreover, the recombination is completely situated at the interface between both EL. Thereby, the exciton density is very high and in consequence, the probability of TTA processes is increased.

In summary, the investigations of red and green OLED employing different host materials in different EL configurations revealed that the concept of a mixed-host EL is a valuable tool to achieve an intrinsically low drive voltage.
6.1.2 Drawback of Mixed-host Emission Layer

The charge carrier balance of mixed-host EL consisting of a constant mixture of a hole- and electron-conducting host material versus EL position is very sensitive to small variations (chapter 3.4) of the mixture ratio and process parameters, as well as drive voltage, luminance and device temperature.

In Fig. 6.4, the luminous efficacy dependence of a red (TER031) OLED (comparable to the organic layer stack of Fig. 6.2 (top-left)) with a mixed-host EL (NPB:TMM004) on the fraction of NPB in the mixed-host is shown. The luminous efficacy is very sensitive to the fraction of NPB and thereby the NPB:TMM004 mixing ratio.

Apart from a change in the host material ratio, a small variation in the injection properties at the electrodes, e.g. caused by different activation of the ITO electrode (chapter 5), can disturb the charge carrier balance considerably.

No matter what causes a change in the charge carrier balance of the device, it can shift the recombination zone so that a quenching at the electrodes or a shift in the color coordinates of a multi-emitter OLED becomes possible. Every change of the luminance and every change of the organic layer stack, like different emitter concentration, would require adjusting the host material ratio to optimize the efficiency again.

6.1.3 Introduction of the Cross-faded Emission Layer

The advantages of a mixed-host EL have to be combined with the stability of e.g. a double EL OLED, in which the recombination zone is always very confined at the interface between the two doped EL.
To increase the lifetime of OLED, in [78] the concept of grading was introduced. Step-by-step, the host material ratio was changed versus EL position. A smoother transition between different organic materials was proposed to increase the device lifetime.

As a further development of a mixed-host EL of constant ratio and the grading concept, a continuous change of the host material ratio versus EL position is introduced in this work. If the host material ratio is continuously changed versus EL position, the concept is termed cross-faded (mixed-host) EL from here-on. As explained in chapter 4.2, the material deposition rates are dependent on the carrier gas flows in an OVPD tool. Thereby, the deposition rate can easily be controlled and continuously changed by MFC. A cross-faded EL can be regarded as the transition between a double EL and a mixed-host EL combining the advantages of both (chapter 3.4).

Exemplarily, the host material curves (NPB and TMM004) in the cross-faded EL zone of Fig. 6.5 symbolize the fraction of each host material at a certain EL position. From the anode to the cathode side of the device, the NPB host material fraction is decreased from 97% vol. to 0% vol., while the fraction of TMM004 is increased from 0% vol. to 97% vol. concurrently. In comparison, a mixed-host EL has a constant ratio of hole- to electron-conducting host material versus zone position. If charge transport in disordered organic materials is described as hopping transport in a Gaussian DOS [8, 10], a change of the host material ratio changes the energetically matching DOS available for hopping transport of holes and electrons. Consequently, the hole and electron mobility is locally changed versus cross-faded EL position.

Along with a decrease from initially high to low charge carrier mobility versus the cross-faded EL position, exciton formation due to charge carrier trapping on emitter molecules becomes probable in a broad part of the EL. This lowers the triplet exciton density (less TTA) and if the EL is doped with different kinds of emitters, offers the possibility to easily tune the emission color (investigated in chapter 6.3). Nevertheless, at the anode side of the EL, only hole conduction and at the cathode side of the device, only electron conduction is possible. This prevents that charge carriers reach the opposite electrode and confines exciton formation to the middle of the cross-faded EL.

If necessary, the host material fraction curves can be changed to manipulate the charge carrier balance of the device or to shift the recombination more to the anode or cathode side of the device. In the case of monochrome red OLED (chapter 7), it is shown that the hole-conducting host material can be completely exchanged without a loss of charge carrier balance or the necessity to adjust the organic layer stack for high efficiency again.

To investigate the functionality of a cross-faded EL, OLED according to the organic layer stack of Fig. 6.5 are processed. The EL is enclosed by a 20 nm NPB HTL and a
50 nm ETM001 ETL. As explained, the material concentration versus EL position is illustrated by the host material fraction curves (NPB and TMM004) in Fig. 6.5.

Fig. 6.5: Organic layer stack of a phosphorescent red OLED with only 2 nm of the 50 nm cross-faded zone doped with CGX150 emitter molecules.

To visualize the recombination zone, only a 2 nm wide part of the 50 nm thick cross-faded zone is doped with CGX150 emitter molecules. Thereby, the emitter molecules act as a tracer for the generation and recombination of excitons in the cross-faded zone. It is assumed that in the middle of the cross-faded zone, in which holes and electrons are both available, the exciton generation and thereby device efficiency (e.g. EQE) is highest (if this area is doped with emitter molecules). Fig. 6.6 illustrates the expected density of holes and electrons and excitons versus the cross-faded zone position.

Fig. 6.6: Illustration of hole, electron and exciton density versus cross-faded zone position.

If the cross-faded zone close to the anode or cathode side of the device is doped with emitter molecules, the device efficiency should be low.

In Fig. 6.7 (right), the EQE at 10 mA/cm² of OLED having the 2 nm doped area at different positions in the cross-faded zone according to Fig. 6.5 and Fig. 6.7 (left) is plotted.
Fig. 6.7: Cross-faded zone (left) and EQE of OLED having the 2 nm doped area at different positions in the zone and idealized host material fractions versus zone position (right).

Fig. 6.7 visualizes the position and thickness of the recombination zone. If a Gaussian function is fitted to the data points, a center-point at a cross-faded zone position of 28 nm and a width of 27 nm can be calculated. The cross-faded zone guarantees a broad but nevertheless restricted recombination zone consistent with the assumptions. Note that in the investigated range, optical effects can be excluded to play a relevant role (based on simulations by LightEX [79]).

For comparison, OLED with a mixed-host zone of constant host material ratio versus zone position are investigated (Fig. 6.8). In the case of a mixed-host, a suitable ratio of hole to electron conductor has to be found to guarantee a charge-balanced device with high efficiency. Consequently, before the position and thickness of the exciton recombination zone can be investigated, the host material ratio (NPB to TMM004) is optimized in terms of efficiency while the 50 nm mixed-host zone is completely doped with CGX150 emitter molecules. A concentration of 37% vol. NPB and 60% vol. TMM004 is found to be suitable. In a further step, comparable to the cross-faded zone in Fig. 6.5, OLED in which only a 2 nm thick part of the mixed-host zone is doped with emitter molecules are processed.
In Fig. 6.9 (right), the EQE at 10 mA/cm$^2$ of OLED having the 2 nm doped area at different positions in the mixed-host zone according to Fig. 6.8 and Fig. 6.9 (left) is plotted.

Compared to the cross-faded OLED, an oppositional behavior can be found. The EQE versus zone position reveals that most of the recombination takes place at the anode side of the EL. In the case of emitters with higher triplet energies than NPB (utilized as 20 nm HTL between anode and EL zone), a quenching of triplet excitons would occur. The emission is not confined to the middle of the EL. The result shows that by
changing the emitter-doped area from 50 nm of the complete mixed-host zone to partially 2 nm, the charge balance can be lost in the case of a mixed-host at constant ratio (compare Fig. 3.14).

In summary, instead of mixed-host EL of constant host material ratio, cross-faded EL with a continuous ratio change versus EL position guarantee a broad but restricted and stable recombination zone.

6.2 Monochrome OVPD OLED

It is known that the process differences between VTE and OVPD prevent the simple transfer of an organic layer stack developed for OLED without adaption from VTE to OVPD tools or vice versa [37]. Before achieving the goal of this work to present white OVPD OLED, organic layer stacks for high-efficiency monochrome OVPD OLED have to be found. Different emitters are investigated (compare with organic material list in Tab. 4.1) and compared in regard to main properties such as efficiency, lifetime and color coordinates. The best suitable emitters are chosen and the results are summarized in Tab. 6.1.

Tab. 6.1: Efficiencies of monochrome OLED at 1000 cd/m² processed by OVPD.

<table>
<thead>
<tr>
<th>OLED</th>
<th>emitter</th>
<th>CIE.x</th>
<th>CIE.y</th>
<th>$\eta_i$ [cd/A]</th>
<th>U [V]</th>
<th>$\eta_P$ [lm/W]</th>
<th>EQE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CGX150</td>
<td>0.61</td>
<td>0.39</td>
<td>30.8</td>
<td>3.3</td>
<td>29.7</td>
<td>18.4</td>
</tr>
<tr>
<td>II</td>
<td>Ir(ppy)$_3$</td>
<td>0.35</td>
<td>0.60</td>
<td>56.2</td>
<td>3.1</td>
<td>56.5</td>
<td>16.1</td>
</tr>
<tr>
<td>III</td>
<td>SEB115</td>
<td>0.15</td>
<td>0.15</td>
<td>8.1</td>
<td>3.8</td>
<td>6.6</td>
<td>4.3</td>
</tr>
</tbody>
</table>

The organic layer stack of OLED-I is shown in Fig. 6.10 and the organic layer stacks of OLED-II/III are shown in Fig. 6.11. Additional information on organic layer stacks of monochrome OVPD OLED can be found in [20] as well.
6. Cross-faded Emission Layer

Fig. 6.10: Organic layer stack of monochrome red (CGX150) OLED-I.

In all organic layer stacks (OLED-I to OLED-III), NPB is utilized as hole injection and transport material. A thickness of 20 nm is commonly chosen. As electron injection material, ETM001 is employed. The thickness of the ETM001 layer is between 20 to 50 nm. If the emission zone is too close to the surface of the metal cathode, plasmonic coupling can be observed [80]. This can lead to a loss in efficiency. Beyond a distance of 200 nm between the metallic cathode and the emission zone, the loss due to plasmon excitation can be neglected. Due to the relatively low mobilities of electron injection and transport materials and the drive voltage increase with increasing ETL thickness, a trade-off has to be found between both effects. The NPB and ETM001 layer enclose the EL.

The red OLED-I (Fig. 6.10) is based on a cross-faded EL which was introduced and explained in the previous chapter. At 1000 cd/m², a luminous efficacy of 29.7 lm/W can be measured. The EQE of 18.4% is close to the maximum value of phosphorescent OLED without any outcoupling enhancements. More information about cross-faded red OLED can be found in [81].

The green OLED-II utilizes the double EL concept, which was introduced and is explained in detail in [37]. The emission takes place at the interface between the Ir(ppy)$_3$-doped TMM004 and the Ir(ppy)$_3$-doped TCTA layer. The double EL is
6. Cross-faded Emission Layer

enclosed by undoped TCTA and TMM004 layers to prevent any triplet exciton diffusion in direction of the NPB and ETM001 layers, in which the excitons would be quenched.

The EL of the fluorescent blue OLED-III is based on a mixture of basically two blue-emitting materials (SEB115 and SMB013). Due to the energy of a blue (400 nm) photon, the gap between the HOMO and LUMO has to be large (>3.1 eV) and it seems to be difficult to synthesize molecules, which conduct both type of charge carriers and have HOMO and LUMO energies in a suitable range to accept charge carriers from common hole and electron transport materials. In the above case, SEB115 is hole-conducting (investigated in chapter 8.2.1) and defined as “Emitter” molecule, while SMB013 is electron-conducting and defined as host (“Matrix”) molecule. Singlet excitons created on SMB013 are transferred via Förster transfer to SEB115. By changing the amount of electrons to holes in the EL, the emission spectrum can be tuned between light-blue and deep-blue color coordinates [20]. Therefore, the 150 nm thick NPB HTL (instead of common 20 nm) of the blue OLED-III is an exception to tune the color coordinates. One possibility to lower the hole density in the EL is a thicker NPB layer which retards the flow of holes. A lower hole density in the EL increases the amount of emission by SMB013 (electron-conducting) and consequently shifts the color coordinates towards deep-blue. Further information about this effect can be found in [20].

The organic layer stacks of OLED-I to OLED-III are optimized for a high efficiency. The highest efficiency and longest lifetime cannot be achieved with the same organic layer stack, but slight modifications (different emitter concentrations, exciton transfer molecules (chapter 7)) are necessary to achieve very long lifetimes. However, applying the same emitter molecules, maximum lifetimes reached are summarized in Tab. 6.2.

**Tab. 6.2:** Lifetimes of monochrome OLED with different emitters.

<table>
<thead>
<tr>
<th>emitter</th>
<th>LT50 [h]</th>
<th>initial brightness [kcd/m²]</th>
<th>extrapolated LT50 @ 1000 cd/m²[h] (n=1.5-1.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGX150</td>
<td>&gt;1200 @ 50 mA/cm²</td>
<td>9.9</td>
<td>50 000-135 000</td>
</tr>
<tr>
<td>Ir(ppy)₃</td>
<td>150 @ 22 mA/cm²</td>
<td>10.0</td>
<td>7000-18 000</td>
</tr>
<tr>
<td>SEB115</td>
<td>&gt;500 @ 50 mA/cm²</td>
<td>3.6</td>
<td>3000-6000</td>
</tr>
</tbody>
</table>

Extrapolations are carried out based on the current density utilizing the Coffin-Manson model (chapter 3.5.4).
Both, efficacy values and lifetimes are comparable with the competing results by e.g. the material suppliers achieved with VTE tools, or if the materials are freely available, with literature [82-83].

6.3 Cross-faded Yellow OLED

In chapter 3.6, different concepts for white emission have been examined and a hybrid setup was chosen for this work. A major challenge is the integration of phosphorescent red and green and fluorescent blue emitters into one organic layer stack. To achieve emission from all emitters, the recombination of charge carriers has to take place at different locations in the organic layer stack. First, it is investigated how the integration of a red and green emitter into one organic layer stack and thereby a yellow color impression can be realized. Later, the yellow-emitting organic layer stack is combined with a fluorescent blue EL to form a hybrid white OLED.

Important requirements of a two-emitter yellow-emitting OLED:

- Easy color coordinate tuning between red and green.
- Highly reproducible color coordinates (process stability).
- Stable color coordinates with changing luminance and device temperature.

In a common organic layer-by-layer stack, the recombination zone is located at interfaces due to mobility and energetic steps. Therefore, it is hard to adjust the color by changing the thickness of the organic layers only. Advantageous would be a broadened recombination zone with the possibility to change the ratio of the red to green doped layer thickness while maintaining the total organic layer stack thickness. A constant total layer thickness would also be beneficial for an optimized outcoupling structure. In chapter 6.1, mixed-host as well as cross-faded EL have been investigated. In the following, both concepts are applied to develop yellow-emitting organic layer stacks.

In Fig. 6.12, a red (TER031) as well as green (Ir(ppy)_3) emitter is integrated into a mixed-host EL at constant ratio of host materials.
6. Cross-faded Emission Layer

Fig. 6.12: Organic layer stack of a yellow OLED based on a mixed-host EL. The solid material curves symbolize the fraction of each material in the EL. The arrow indicates a shift in the red to green doped area.

The 20 nm HTL (NPB) is followed by a 40 nm EL consisting of a constant mixture of the hole (bipolar-conducting) transport material CBP and electron transport material TMM004. One part of the EL is doped with TER031 (red emitter) while the second part is doped with Ir(ppy)$_3$ (green emitter). The electron injection layer consists of ETM001. CBP and TMM004 have different mobilities for holes and electrons. For a well charge-balanced device, the host material ratio has to be adjusted. 15% vol. of TMM004 and 80% vol. of CBP are found to be suitable. A higher fraction of TMM004 would shift the recombination to the anode side of the device due to favored electron conduction and would result in red emission only.

In Fig. 6.13, instead of the mixed-host EL of Fig. 6.12, a cross-faded EL based on the same materials is shown. Compared to Fig. 6.12, only the EL is changed.

Fig. 6.13: Organic layer stack of a yellow OLED based on a cross-faded EL. The solid material curves symbolize the fraction of each material in the EL. The arrow A indicates a shift in the red to green doped area. The arrow B indicates an exemplary slope adjustment of the CBP fraction curve from the dashed to solid blue line.
Again, due to the different mobilities in CBP and TMM004, the host material fractions have to be adjusted in the case of a cross-faded EL as well. Exemplarily, this is shown in Fig. 6.13 at point B (end concentration of CBP at ETM001 interface). The best efficiencies can be measured if the concentration of CBP decreases linearly from 95% vol. to 65% vol. versus the cross-faded EL while the concentration of TMM004 increases from 0% vol. to 30% vol..

Both organic layer stacks (mixed-host and cross-faded) are now compared in terms of efficiency and stability.

6.3.1 Comparison of Mixed-host and Cross-faded yellow OLED

Yellow-emitting OLED according to Fig. 6.12 and Fig. 6.13 are processed applying the described host material concentrations. The ratio between the red and green doped area is varied according to arrow A in Fig. 6.12 and Fig. 6.13. The measurement results are summarized in Tab. 6.3.

<table>
<thead>
<tr>
<th>OLED</th>
<th>red:green [nm:nn]</th>
<th>CIEx/CIEy</th>
<th>curr. eff. [cd/A]</th>
<th>lum. eff. [lm/W]</th>
<th>EQE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-CF</td>
<td>00:40</td>
<td>0.32/0.62</td>
<td>50.9</td>
<td>39.7</td>
<td>14.3</td>
</tr>
<tr>
<td>2-CF</td>
<td>05:35</td>
<td>0.37/0.58</td>
<td>51.1</td>
<td>41.0</td>
<td>15.8</td>
</tr>
<tr>
<td>3-CF</td>
<td>10:30</td>
<td>0.47/0.50</td>
<td>42.2</td>
<td>32.9</td>
<td>16.2</td>
</tr>
<tr>
<td>4-CF</td>
<td>15:25</td>
<td>0.56/0.43</td>
<td>33.9</td>
<td>26.3</td>
<td>16.2</td>
</tr>
<tr>
<td>5-CF</td>
<td>20:20</td>
<td>0.62/0.39</td>
<td>30.1</td>
<td>21.6</td>
<td>16.6</td>
</tr>
<tr>
<td>6-MH</td>
<td>05:35</td>
<td>0.43/0.53</td>
<td>33.3</td>
<td>24.8</td>
<td>11.8</td>
</tr>
<tr>
<td>7-MH</td>
<td>10:30</td>
<td>0.51/0.47</td>
<td>27.5</td>
<td>19.7</td>
<td>11.6</td>
</tr>
<tr>
<td>8-MH</td>
<td>15:25</td>
<td>0.57/0.42</td>
<td>23.1</td>
<td>15.5</td>
<td>11.5</td>
</tr>
</tbody>
</table>

OLED-1-CF to OLED-5-CF are based on a cross-faded EL, whereas OLED-6-MH to OLED-8-MH are based on a mixed-host EL. In Fig. 6.14, the color coordinates of the OLED are visualized.
6. Cross-faded Emission Layer

The color coordinates can be shifted between pure red and green emission while the EQE of the cross-faded devices remains around 16%. The color coordinate shift visualizes the location of recombination zone. It is advantageous to confine it between the HTL-to-EL interface and the middle of the cross-faded zone. Excitons created on green emitter molecules diffusing in direction of the anode side of the device are harvested by red emitter molecules. In the case of a diffusion to the cathode side of the device they can decay on other green emitter molecules before they reach the cathode. Exciton diffusion from red emitter molecules is not possible due to higher triplet energies of all other materials. The EQE of the optimized mixed-host devices is around 11%, which is lower compared to the cross-faded devices. If the recombination zone is not confined to the middle of the mixed-host EL, the diffusion of triplet excitons from green emitter to ETM001 molecules at the cathode side of the device becomes possible. Consequently, the triplet excitons decay non-radiatively and the EQE is lowered.

To investigate the color coordinate stability versus luminance, spectra of OLED-3-CF and OLED-6-MH are taken at 200, 1000, 5000 and 10 000 cd/m² and the according color coordinates are visualized in Fig. 6.15.

![Fig. 6.14: Color coordinate plot of OLED of Tab. 6.3.](image)
Fig. 6.15: Color coordinate plot of OLED-3-CF and OLED-6-MH at different luminance.

An excellent color coordinate stability versus luminance can be found for OLED-3-CF, indicating a well charge-balanced device. Compared to OLED-3-CF, OLED-6-MH has unstable color coordinates versus luminance. The more the luminance is increased, the more are the color coordinates shifted towards green. The recombination zone shifts towards the cathode with increasing luminance and promotes the amount of green emission.

To get an insight in possible additional exciton losses, the color coordinates of OLED-2,3,4-CF are reproduced by numerically weighting and combining the spectra of the monochrome OLED-1,5-CF. The weighting factors are then applied to the current efficacy values of OLED-1,5-CF and the weighted sum is compared to the current efficacy value of OLED-2,3,4-CF. The calculated values are up to 10% lower than the measured ones. This indicates that no further exciton loss channels exist in the structure and the cross-faded EL is a well-controllable concept.

OLED-4-CF and OLED-8-MH exhibit the same color coordinates, so that quantitatively, a direct comparison is possible. The current efficacy of OLED-8-MH is by 32% lower than the one of OLED-4-CF. The calculation of the true current efficacy of the pure red OLED-5-CF results in 205 cd/A and of the pure green OLED-1-CF results in 352 cd/A. The current efficacy of the red OLED is 42% less compared to the green OLED. Taking into account the lower current efficacy of OLED-8-MH compared to OLED-4-CF, stronger exciton diffusion from green to red emitter molecules in the mixed-host device must be present.
Tab. 6.4 compares and summarizes the properties of mixed-host and cross-faded yellow EL discussed beforehand.

**Tab. 6.4**: Comparison of properties of mixed-host and cross-faded yellow EL.

<table>
<thead>
<tr>
<th></th>
<th>mixed-host EL + ETL</th>
<th>cross-faded EL + ETL</th>
</tr>
</thead>
<tbody>
<tr>
<td>@ 1 kcd/m²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reduced current efficacy</td>
<td>reduced EQE</td>
<td></td>
</tr>
<tr>
<td>red:green ratio shifted to green</td>
<td>less triplet diffusion</td>
<td>no triplet diffusion</td>
</tr>
<tr>
<td>color coordinates shifted towards green (less compared to cross-faded EL)</td>
<td>color coordinates shift towards green</td>
<td>EQE increases slightly due to less triplet quenching in ETM001</td>
</tr>
<tr>
<td>luminance increased to 10 kcd/m²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>color coordinates shifted towards green</td>
<td>no change in color coordinates</td>
<td></td>
</tr>
</tbody>
</table>

In summary, a cross-faded EL offers the possibility to adjust the color coordinates of a yellow OLED easily between red and green at a constantly high EQE and with highly stable color coordinates versus changing luminance. The recombination zone can be confined in a well defined range. The two-emitter organic layer stack validates the performance of a cross-faded EL.
7 Exciton Transfer for Lifetime Enhancement

In this chapter, the lifetime of monochrome red OLED and possible physical limitations are investigated in detail. A new concept to increase the lifetime is presented and demonstrated applying it to different red emitters.

7.1 Accelerated Lifetime Measurement

With the lifetime of red OLED approaching several ten thousand hours at standard low luminance (1000 cd/m\(^2\)) the lifetime measurement obviously has to be accelerated. According to chapter 3.5.4, the Coffin-Manson model can be applied to extrapolate lifetime data. The lifetime can be measured at high luminance and extrapolated to standard low luminance. However, the acceleration factors (equation (3.13)) for the current and power density have to be known. To be able to neglect the influence of the power density, but to guarantee an as fast as possible lifetime measurement, it has to be investigated, up to which value the power density can be increased without influencing the lifetime.

In our group [50], the influence of current and power density was investigated utilizing the lifetime measurement station shown in Fig. 3.16. The extension to pulsed-mode operation (chapter 3.5.4) allowed separating the influence of the current and power density on lifetime. Up to a power density of 300 mW/cm\(^2\), no influence on OLED lifetime can be found and the acceleration factor describing the power density in equation (3.13) is \(n_p=0\). Consequently, the device temperature has no influence on the degradation. At higher power densities, \(n_p>0\) is found. If the current density is changed and the power density is kept below 300 mW/cm\(^2\), a constant acceleration factor \(n_j\) is found. The Coffin-Manson model is proven to be suitable to describe the degradation caused by the current density. Note that the power density limit, which prevents temperature-induced degradation, is only true for the same geometric device architecture (Stargate substrate, compare chapter 4.3.2) and under the same measurement conditions (e.g. surface material of the measurement station). If the organic layer stack is changed, \(n_p\) could change as well, but probably stays valid to
some extent if the same organic materials are involved. In the following, lifetime measurements are performed keeping the power density under or around 300 mW/cm$^2$ to prevent a temperature-dependent degradation. OLED are measured at constant current density and if necessary in pulsed-mode operation.

7.2 Lifetime of Monochrome Red (CGX150) OLED

Lifetimes approaching 800 h can be found in literature [84-85] for phosphorescent red OLED driven at high luminance of around 10,000 cd/m$^2$. The goal is therefore to present red OLED having lifetimes in a comparable range or even better. Considering the white OLED to be developed, a high lifetime should be realized not only with low-triplet energy host materials (e.g. NPB) but with high-triplet energy host materials (e.g. TCTA, TMM004) as well.

Fig. 7.1 shows the basic organic layer stack of a monochrome red-emitting OLED which is employed to investigate the lifetime of different red emitters and different hole-conducting host materials. Exemplarily, CGX150 is used as red emitter.

![Fig. 7.1: Organic layer stack of red OLED.](image)

The lifetime is measured investigating NPB as hole-conducting host material, as well as TMM117 and TCTA instead. TMM117 and TCTA have sufficiently high triplet energies to be a host material for Ir(ppy)$_3$. Therefore, both could be employed in the cross-faded zone (yellow-emitting part) of a white OLED. In Tab. 7.1 (part A), the efficiency values of the investigated red-emitting OLED are listed.
Tab. 7.1: Comparison of OLED with the EL based on different hole-conducting host materials (NPB, TMM117, TCTA and TCTA:Ir(ppy)_3) and CGX150 as emitter.

<table>
<thead>
<tr>
<th>part</th>
<th>OLED</th>
<th>@ 1000 cd/m²</th>
<th>@ 50 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>curr. eff.</td>
<td>voltage</td>
<td>lum. eff.</td>
</tr>
<tr>
<td></td>
<td>[cd/A]</td>
<td>[V]</td>
<td>[lm/W]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1-NPB</td>
<td>31.6</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>2-TMM117</td>
<td>27.5</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>3-TCTA</td>
<td>26.6</td>
<td>3.4</td>
</tr>
<tr>
<td>B</td>
<td>4-Ir(ppy)_3 (5%)</td>
<td>31.9</td>
<td>3.3</td>
</tr>
<tr>
<td>(based on 5-Ir(ppy)_3 (15%)</td>
<td>31.6</td>
<td>3.4</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td>6-Ir(ppy)_3 (25%)</td>
<td>30.0</td>
<td>3.4</td>
</tr>
</tbody>
</table>

The current efficacy at 1000 cd/m² of all OLED is in the range of 26.6 to 31.9 cd/A while the drive voltage is in a range of 3.0 to 3.4 V. The TMM117-based OLED-2-TMM117 has a drive voltage of 4.2 V, which is an exception due to the lower hole mobility of TMM117 in comparison to NPB and TCTA.

The lifetime is measured at 50 mA/cm² and listed in Tab. 7.1 as well. Depending on the employed hole transporter, the lifetime differs by up to one order of magnitude. For OLED-1-NPB, based on NPB, 149 h can be measured, whereas for OLED-3-TCTA, based on TCTA, only 15 h can be measured. OLED-2-TMM117 utilizing TMM117 has a lifetime of 51 h.

To clarify if the difference in lifetime results from the different properties of the hole transporter or an interaction of the hole transporter and the emitter, a different red emitter is investigated.

7.2.1 Lifetime of Monochrome Red (TER031) OLED

The lifetime is measured again after CGX150 is replaced by TER031 in the organic layer stack of Fig. 7.1 utilizing NPB and TCTA as hole-conducting host materials. In comparison to CGX150, the lifetime of TER031 is assumed to be relatively lower (according to the material supplier).

At a constant current density of 50 mA/cm², a lifetime of 42 h can be measured if NPB as hole-conducting host material is utilized and only 7 h in the case of TCTA.

The reduction in lifetime if TCTA instead of NPB is utilized as hole-conducting host material is qualitatively the same for the two different phosphorescent red emitters (CGX150 (reduction to 10%) and TER031 (reduction to 17%)).
One probable factor which can deteriorate the lifetime is therefore a lower stability of the hole-conducting host material TCTA.

### 7.3 Applying Exciton Transfer Molecules

It is known that the common and long-lasting electron conductor Alq₃ can become instable if it is oxidized [44, 46]. Cationic Alq₃ species can dissociate and their degradation products are non-radiative recombination centers and act as fluorescence quenchers.

Recently, the dissociation of TCTA anions in phosphorescent blue OLED has been investigated [86]. TCTA degradation fragments can react and furthermore act as emission quenchers. This finding supports the assumption of instable TCTA molecules.

If a generalization is possible, unipolar-conducting host molecules seem to be sensitive to the charge carrier type they are not well-conducting. The chemical instability of TCTA is probably the reason for the short lifetime.

To further investigate this possibility, the EL of OLED-3-TCTA of Tab. 7.1 is doped with an additional fraction of Ir(ppy)₃ at different concentrations. OLED-4,5,6-Ir(ppy)₃ are doped with 5% vol., 15% vol. and 25% vol. of Ir(ppy)₃, respectively. The current efficacy and drive voltage do not change significantly compared to OLED-3-TCTA (Tab. 7.1 (part B)).

If in the following the lifetime is measured at a current density of 50 mA/cm² for OLED-4,5,6-Ir(ppy)₃, 66 h, 216 h and 387 h can be measured. The lifetime of OLED-6-Ir(ppy)₃ is improved by a factor of 26 compared to OLED-3-TCTA and the lifetime is even higher than the one of OLED-1-NPB. The lifetime as well as luminous efficacy of OLED-3 to OLED-6 are plotted in Fig. 7.2 (left). Up to an additional Ir(ppy)₃ concentration of 25%, no saturation in the increase of lifetime can be seen. However, with increasing Ir(ppy)₃ concentration, the luminous efficacy begins to decrease slowly and it is not possible to investigate a higher concentration due to constraints in the possible deposition rate ratio. Devices without any TCTA but a pure mixture of TMM004:CGX150 or TMM004:Ir(ppy)₃:CGX150 have been investigated and found not to be competitive in terms of efficiency.
7. Exciton Transfer for Lifetime Enhancement

Fig. 7.2: Lifetime and luminous efficacy of OLED-3 to OLED-6 of Tab. 7.1 (left). HOMO and LUMO energies employing TCTA and Ir(ppy)$_3$ in the EL (right). Triplet energy transfer from Ir(ppy)$_3$ to CGX150 (inset).

In Fig. 7.2 (right), the HOMO and LUMO energies of the Ir(ppy)$_3$-doped OLED are shown. Ir(ppy)$_3$ acts as a stabilizing molecule. It is concluded that the LUMO of Ir(ppy)$_3$, which is situated between the one of TCTA and TMM004 can prevent a possible chemical reduction and degradation of TCTA molecules. Thereby, the creation of non-radiative recombination centers is suppressed and the lifetime increases significantly. Due to the LUMO energy of NPB and Ir(ppy)$_3$, it is not possible to protect NPB via the same mechanism, but in comparison, NPB seems to be more stable against a chemical reduction than TCTA.

Considering that the lifetime of the TCTA-based OLED-6-Ir(ppy)$_3$ is even more than doubled compared to the one of OLED-1-NPB, another mechanism could additionally exist helping to increase the lifetime. Two mechanisms are straightforward to generate excitons on red emitter molecules: Direct charge carrier trapping on the red emitter or the diffusion of triplet excitons from the host to the emitter. As soon as Ir(ppy)$_3$ is added to the EL, an exciton formation becomes possible on it, followed by an exciton transfer to CGX150 (Fig. 7.2 (right) (inset)). Due to the HOMO of Ir(ppy)$_3$ compared to the HOMO of TCTA, exciton formation is likely to happen on Ir(ppy)$_3$. Concurrently, this would enhance the electron capture on Ir(ppy)$_3$ before TCTA could be reduced by electrons out of the TMM004 LUMO. It is proposed that in consequence the exciton diffusion from Ir(ppy)$_3$ to CGX150 stresses the red emitter less than a direct charge carrier trapping on CGX150 molecules (like in OLED-1-NPB to OLED-3-TCTA). However, no green emission is visible in the spectra so that the exciton transfer from Ir(ppy)$_3$ to the red emitter has to be very fast.

In conclusion, to prevent the reduction of the hole-conducting host molecules (e.g. possible in the case of TCTA) combined with triplet formation on the emitter by diffusion (e.g. from Ir(ppy)$_3$ and instead of charge carrier trapping), increases the
lifetime of red OLED significantly. If \( \text{Ir(ppy)}_3 \) molecules are employed to increase the lifetime as explained, they are defined as *exciton transfer molecules* from now on.

### 7.4 Lifetime Extrapolation

To extrapolate the lifetime of OLED-6-Ir(ppy)_3, different devices with the same organic layer stack are driven at different current densities. According to the Coffin-Manson model (see equation (3.13)), the acceleration factor can be graphically determined by a linear fit in Fig. 7.3 to \( n=1.9 \).

![Fig. 7.3: Lifetime of OLED-6-Ir(ppy)_3 at different current densities and linear fit.](image)

Extrapolated to a luminance of 1000 cd/m², a lifetime of more than 60 000 h can be calculated for OLED-6-Ir(ppy)_3.

If the concept of exciton transfer molecules is applied to OLED-2-TMM117 (additionally 15% vol. of \( \text{Ir(ppy)}_3 \) are added to the EL), a lifetime of 1174 h can be measured (at 50 mA/cm² and an initial luminance of 9.9 kcd/m²). If an acceleration factor of \( n=1.9 \) is assumed, according to the Coffin-Manson model, a lifetime of more than 130 000 h can be calculated for 1000 cd/m². Compared with scientific literature ([85]: ~50 kh), this is probably the highest value reported for CGX150 (Ir(MDQ)_2(acac)).
### 7.5 Lifetime Comparison of Different Red Emitters

Applying the concept of exciton transfer molecules to different red-emitting molecules, the lifetime is investigated for CGX150, Ir(piq)$_3$ (compare with organic materials in Tab. 4.1) and TER031 with an additional fraction of 25% vol. of Ir(ppy)$_3$ added to the EL. The basic organic layer stack can be found in Fig. 7.1 but with TCTA instead of NPB as hole-conducting host material.

**Tab. 7.2: Comparison of red OLED with different red emitters (CGX150, Ir(piq)$_3$ and TER031) and exciton transfer molecules (Ir(ppy)$_3$).**

<table>
<thead>
<tr>
<th>OLED</th>
<th>curr. eff. @ 1000 cd/m$^2$ [cd/A]</th>
<th>voltage @ 1000 cd/m$^2$ [V]</th>
<th>lum. eff. @ 1000 cd/m$^2$ [lm/W]</th>
<th>initial luminance @ 50 mA/cm$^2$ [kcd/m$^2$]</th>
<th>lifetime @ 50 mA/cm$^2$ [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-CGX150</td>
<td>30.0</td>
<td>3.4</td>
<td>27.5</td>
<td>12.8</td>
<td>387</td>
</tr>
<tr>
<td>B-Ir(piq)$_3$</td>
<td>11.1</td>
<td>3.9</td>
<td>8.8</td>
<td>3.9</td>
<td>331</td>
</tr>
<tr>
<td>C-TER031</td>
<td>31.9</td>
<td>4.0</td>
<td>25.2</td>
<td>13.9</td>
<td>80</td>
</tr>
</tbody>
</table>

All investigated red phosphorescent emitters can be stabilized in a high-triplet energy host material mixture (TCTA:TMM004) employing exciton transfer molecules.

OLED-B-Ir(piq)$_3$ is based on the deep-red emitter Ir(piq)$_3$ having color coordinates of 0.66/0.34. Due to the mismatch between the emission spectra of OLED-B-Ir(piq)$_3$ and the eye sensitivity function (Fig. 7.4), the current efficacy is low. In Fig. 7.4, the part of the red OLED spectrum at which the human eye sensitivity decreased below relative 10% of its maximum value is highlighted.

**Fig. 7.4:** Comparison of the eye sensitivity function and spectrum of red (Ir(piq)$_3$) OLED.
A large amount of the emission is lost in this sense and does not contribute to the luminance. Nevertheless, the emitter and organic layer stack work well having an EQE of 12.7% (OLED-B-Ir(piq)$_3$).
8 Hybrid White OVPD OLED

In this chapter, the investigations of chapter 5 (Study of Interface Stabilization), chapter 6 (Cross-faded Emission Layer) and chapter 7 (Exciton Transfer for Lifetime Enhancement) are combined to create a hybrid white OVPD OLED. The measurement results and the progress beyond state-of-the-art are discussed and the potential for further development is described.

8.1 Separation of Yellow and Blue Emission

To achieve white light emission, a phosphorescent yellow EL is combined with a fluorescent blue EL. The fluorescent blue-emitting part consists of the host material SMB013 and the blue emitter SEB115 (compare with organic materials in Tab. 4.1). A monochrome blue OLED based on the same organic materials was presented in 6.2. The according organic layer stack was shown in Fig. 6.11 (right). To further investigate the properties of SMB013 and SEB115, electron- and hole-only devices are processed according to Fig. 8.1.

![Fig. 8.1: Electron-only (left) and hole-only (right) device investigating SMB013 or SEB115.](image_url)

The HOMO and LUMO energies of the organic layer stacks of these single-carrier devices are chosen to allow only one type of charge carrier to be conducted by the organic material to be investigated (e.g. SMB013 or SEB115). Fig. 8.2 visualizes the concept and energetic barriers. The HOMO and LUMO energies of TMM004, ETM001 and NPB either prevent or promote the injection of one type of charge carrier. Additionally, these organic materials only conduct one type of charge carrier preferentially.
Even if the investigated organic material was bipolar conducting, the properties of hole and electron conduction could be independently determined. Due to the absence of both types of charge carriers, recombination processes can be neglected.

In Fig. 8.3, the current density of the devices is plotted versus voltage.

SMB013 is electron-conducting while SEB115 is hole-conducting. If the blue EL was situated at the anode side of the white OLED, SEB115 molecules would not only have to act as emitter but as hole transport molecules as well. To be able to choose the SEB115 emitter fraction independently and without regard to the charge carrier...
balance of the complete white OLED, the blue-emitting layer will be situated at the cathode side of the device. Concurrently, this prevents a possible preterm degradation of SEB115 molecules due to excessive hole transport. However, this has not been investigated. Electrons are conducted by the SMB013 host and a large fraction of them can pass through the blue EL to reach the phosphorescent yellow EL.

It has to be avoided that the phosphorescent and fluorescent EL are in direct contact to each other. The reason can be found in the very low triplet energy of SMB013. To qualitatively investigate the triplet energy of SMB013 and SEB115, a small fraction of the materials is independently doped into the EL of a phosphorescent red (TER031) OLED (chapter 6.2). The triplet energy of the phosphorescent red emitters TER031 and CGX150 can be assumed to be the same due to a large overlap in emission spectra. In the presence of SMB013, the red emission is nearly quenched completely, while in the presence of SEB115, the current efficacy decreases to around 50%. The triplet energies are qualitatively shown in Fig. 8.4 (left).

**Fig. 8.4:** Qualitative triplet energies of the employed organic materials (left) and possible arrangement in the organic layer stack of the white OLED (right).

Between the phosphorescent yellow-emitting part and the fluorescent blue-emitting part of the white OLED, an interlayer consisting of a mixture of the electron-conducting material TMM004 and the hole-conducting material TCTA is inserted (compare triplet energies in organic layer stack in Fig. 8.4 (right)). The bipolar-conducting host material CBP, which was employed in chapter 6.3 as hole conductor in yellow OLED, is replaced by TCTA due to its better hole mobility. Additionally, TCTA is only unipolar-conducting so that the electron and hole conduction is strictly limited to different kinds of molecules.

A mixed-host interlayer is advantageous compared to an interlayer consisting of only one bipolar-conducting host material like CBP. If holes and electrons are conducted by different kinds of molecules, it is less likely that excitons are formed and recombine non-radiatively. In [87], hybrid white OVPD OLED employing CBP as bipolar
interlayer material were investigated. The luminous efficacy at warm-white color coordinates is around 13 lm/W (at 1000 cd/m²), which is significantly less than the later-on discussed efficacy of a mixed-host interlayer approach.

### 8.2 Final Organic Layer Stack

All important parts of a hybrid white OVPD OLED are investigated and consequently, in Fig. 8.5, the combination to the final organic layer stack is shown. Integrated in the organic layer stack is the concept of a cross-faded phosphorescent yellow EL, a phosphorescent to fluorescent interlayer and the usage of exciton transfer molecules.

**Fig. 8.5:** Organic layer stack of developed hybrid white OVPD OLED and points of interest.

The important points of interest and according investigations are numbered:

1. Study of Interface Stabilization (chapter 5)
2. Cross-faded Emission Layer (chapter 6)
   and Cross-faded Yellow OLED (chapter 6.3)
3. Separation of Yellow and Blue Emission (chapter 8.1)
4. Electron-Blocking Layer (chapter 8.2.1)
5. Color Coordinate Tuning and Stability (chapter 8.2.2)
6. Lifetime of White OLED (chapter 8.3)

Points 1 to 3 have been discussed in the previous chapters, while points 4 to 6 are investigated in the following chapters.

The organic layer stack in Fig. 8.5 consists of a 40 nm NPB HTL, a 20 nm cross-faded phosphorescent yellow EL, a 10 nm fluorescent blue EL and a 5 nm electron-blocking TMM004 layer, followed by a 40 nm ETM001 ETL. 9 nm of the yellow EL are doped with CGX150 and exciton transfer molecules (Ir(ppy)₃), followed by 7 nm doped with...
Ir(ppy)$_3$ and a 4 nm thick triplet-blocking interlayer. The ratio between the red and green doped area can be easily adjusted to tune the emission color. The HOMO/LUMO energy distribution can be derived from Fig. 8.5 and is plotted in Fig. 8.6.

![Fig. 8.6: HOMO and LUMO energies of the employed organic materials of the white light-emitting organic layer stack of Fig. 8.5.](image)

Note that the energy levels in Fig. 8.6 taken from Tab. 4.1 describe individual measurements. Any kind of dipole layers or doping effects altering the energy levels cannot be reproduced by the individually measured values. This would require in-situ UPS measurements during processing. Nevertheless, the individual energy levels already provide an insight in the energetic structure of the organic layer stack.

Holes are injected from the ITO into the NPB layer and transported to the yellow EL. Due to the mixture of the hole conductor TCTA and electron conductor TMM004 in the cross-faded yellow EL, a part of the holes is transported further to the blue EL. Electrons are injected into the ETM001 layer and are transported in part by SMB013 to the yellow EL concurrently. The TMM004 electron-blocking layer at the cathode side of the device is investigated in the following chapter.

### 8.2.1 Electron-Blocking Layer

One important part of the organic layer stack of the hybrid white OLED of Fig. 8.5 is the electron-blocking TMM004 layer situated between the blue EL and the ETM001 electron injection and transport layer. Without the electron-blocking layer, it is not possible to achieve white color coordinates. In Fig. 8.7, the color coordinates of white OLED having different TMM004 layer thicknesses are shown.
At a TMM004 layer thickness of more than 3 nm, OLED having a white color impression can be achieved.

How does the TMM004 layer work? SMB013, TMM004 and ETM001 are all good electron conductors and their LUMO energies are close to each other (compare Tab. 4.1 or Fig. 8.6). A difference in LUMO energies can therefore not explain an electron-blocking behavior. Nevertheless, it is not possible to explain the extreme blue-shift without an electron-blocking effect. To get an insight in the electron-blocking capabilities, the fluorescent blue-emitting part is investigated separately. Electron-only devices according to Fig. 8.8 (left) are processed with and without a TMM004 layer.

![Fig. 8.7: Color coordinates if the TMM004 electron-blocking layer thickness is increased.](image)

![Fig. 8.8: Electron-only devices with and without 10 nm TMM004 blocking layer (left). Current density versus voltage for these electron-only devices (right).](image)
In Fig. 8.8 (right), the current density versus voltage of the described electron-only devices is plotted. Due to the additional TMM004 layer, the current density is decreased by 4 orders of magnitude.

The TMM004/ETM001 interface cannot cause this decrease. In many of the investigated OLED, a TMM004/ETM001 interface is present, but like in monochrome red OLED, very low drive voltages can be measured at 1000 cd/m². If ETM001 is replaced by another common electron transport and injection material like Alq₃, the same blocking behavior can be observed.

The effect has to be caused by an interaction of SMB013 and TMM004. It is assumed that an electron-blocking dipole layer is created at the SMB013/TMM004 interface. Due to the accumulation of negative charges, holes are attracted and forced to penetrate deeper in the blue EL, or respectively, at a certain current, the retardation of electrons increases the amount of holes which are transported in direction of the cathode. Consequently, the amount of blue emission increases. The effect saturates with increasing TMM004 layer thickness. This is expected, because the effect of charge accumulation or retardation should not be thickness-dependent, but rather saturating as soon as a closed and energetically homogeneous interface (>10 nm) is formed.

8.2.2 Color Coordinate Tuning and Stability

It was shown that the thickness of the TMM004 layer can control the amount of blue emission significantly. Furthermore, according to chapter 6.3.1, the color coordinates should be tunable between red and green simply by changing the red to green doped area in the cross-faded phosphorescent EL. This is visualized in Fig. 8.9.

**Fig. 8.9:** Color coordinates if the red to green doped area is changed by 1 nm at a TMM004 layer thickness of 5 nm.
The red to green doped area is changed by only 1 nm to shift the color coordinates effectively towards green or red. This indicates that the recombination maximum with regard to the yellow emission is situated in the middle of the cross-faded phosphorescent EL.

Next, it is investigated, how the color coordinates change if the luminance is increased from 1000 to 10 000 cd/m². The color coordinates are listed in Tab. 8.1.

**Tab. 8.1:** Color coordinates at increasing luminance.

<table>
<thead>
<tr>
<th>Luminance [cd/m²]</th>
<th>CIEx</th>
<th>CIEy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.371</td>
<td>0.363</td>
</tr>
<tr>
<td>2000</td>
<td>0.378</td>
<td>0.368</td>
</tr>
<tr>
<td>5000</td>
<td>0.381</td>
<td>0.372</td>
</tr>
<tr>
<td>10 000</td>
<td>0.378</td>
<td>0.372</td>
</tr>
</tbody>
</table>

The color coordinates are stable with increasing luminance (1000 to 10 000 cd/m²: ΔCIEx and ΔCIEy ≤ 0.01). Thus, the white OLED fulfills the stability requirement for color coordinates of Tab. 2.2 and is suitable for dimmable white light illumination. The color temperature impression is maintained.

### 8.3 Lifetime of White OLED

First, the lifetime of white OLED according to the organic layer stack of Fig. 8.5, but without the application of exciton transfer molecules is investigated utilizing the setup described in chapter 3.5.4.

At a current density of 50 mA/cm² the luminance decreases to 50% if its initial value (9.8 kcd/m²) in 8.7 h. Fig. 8.10 (left) visualizes the normalized intensity versus wavelength of the OLED before and after lifetime measurement.
After 8.7 h of operation, the emission characteristic has changed significantly. In relation to the blue (SEB115) emission peak, both, the green (Ir(ppy)$_3$) but even more the red (CGX150) emission peak decreased significantly. The ratio of the red emission peak before and after lifetime measurement can be calculated to 1/3. The color coordinates of the OLED shifts from warm-white to cold-white.

Following, the concept of exciton transfer molecules is transferred to the white OLED organic layer stack. To increase the lifetime, 20% vol. of Ir(ppy)$_3$ are added to the phosphorescent red emitter doped area in accordance with Fig. 8.5. The lifetime at 50 mA/cm$^2$ (initial luminance: 10.9 kcd/m$^2$) increases from 8.7 h to 24.5 h, which is nearly tripled and proves the functionality of the exciton transfer concept. However, at the end of OLED lifetime after 24.5 h, the main decrease in luminance is still caused by the green and red emission peaks. The ratio of the red emission peak before and after lifetime measurement can be calculated to 1/2. The lifetime at 1000 cd/m$^2$ can be estimated to 1100-2900 h ($n=1.5-1.9$).

As shown in Fig. 8.5, the interlayer consists of TCTA and TMM004. TCTA is not protected by exciton transfer molecules in the interlayer. TCTA molecules can degrade and degradation products can act as triplet exciton quencher for adjoining Ir(ppy)$_3$ molecules and as charge carrier traps. Because both, the green as well as red emission decrease, probably electrons are trapped in the interlayer and the non-radiative recombination increases. Concurrently, less excitons can be generated in the phosphorescent yellow EL.

### 8.4 Discussion of White OLED Data

To estimate the possible efficiency of the presented hybrid white OVPD OLED, the efficiency values of the monochrome OLED of chapter 6.2 are taken. The spectra of the
monochrome OLED are scaled and combined in such a way that the summation represents a white emission with color coordinates of 0.45/0.42. Next, the amount of photons supplied by each emitter to the total spectrum is calculated. The ratio between the different emitters is determined and the factors are applied to the current efficacies of the monochrome OLED. In Fig. 8.11, the scaled spectra of the monochrome OLED as well as the summation are shown. The percentage values describe the amount of photons supplied by each emitter to the total spectrum.

![Fig. 8.11: Scaled spectra of monochrome OLED and the calculated summation.](image)

In total, a theoretical maximum current efficacy of 36 cd/A can be calculated. If a minimum drive voltage of 3.1 V (400 nm photon) is assumed, a luminous efficacy of at best 36 lm/W could be reached. The calculation assumes a Lambertian emission as well as an unchanged outcoupling efficiency if the monochrome OLED are combined to a white OLED. In reality, the organic layer stacks of the monochrome OLED are tuned to guarantee an as high as possible efficiency. If the emitters are integrated in the white OLED organic layer stack, all optical and electrical properties have to be balanced to achieve white emission. Consequently, a compromise has to be made and the maximum achievable efficiency is lowered. Additionally, reabsorption and triplet transfer and quenching processes can lower the efficiency as well.

A current efficacy and drive voltage of 24.7 cd/A and 3.6 V can be measured for the presented white OLED according to Fig. 8.5 at 1000 cd/m². If these values are compared with the estimated value of 36 cd/A and assumed value of 3.1 V, the achieved values are 31% lower and 16% higher.

In chapter 6.3.1, the current efficacy of monochrome red and green OLED was taken to estimate the current efficacy of yellow OLED and compared with the measured values
of the developed cross-faded yellow OLED. The measured values were equal or even higher than the calculated ones.

In conclusion, the loss of 31% in current efficacy of a multilayer hybrid white OLED stack most probably is caused by the insertion of the fluorescent blue EL. Besides the absorption of blue photons by red or green emitter molecules, unwanted non-radiative recombination of charge carriers in the separating interlayer cannot be avoided completely.

The higher drive voltage is a result of the TMM004 electron-blocking layer (chapter 8.2.1) which is necessary to achieve blue emission.

In Fig. 8.12, the spectrum of the white OLED and the emission peaks of the 100%-efficient light source (chapter 3.6.1) are shown. The central wavelength of the employed blue (SEB115) and red (CGX150) emitter match well with the peaks of the 100%-efficient light source. The central wavelength of the green (Ir(ppy)$_3$) emitter instead is too blue-shifted and does not overlap with the greenish peaks of the 100%-efficient light source (and the maximum of the eye sensitivity function). One possibility to further increase the efficiency of the white OLED would be to employ a more suitable green emitter.

![Fig. 8.12: Spectrum of hybrid white OVPD OLED and emission peaks of 100%-efficient light source.](image)

One major advantage of organic semiconductors is their relatively broad emission spectrum in contrast to inorganic semiconductors. Thereby, it is relatively easy to achieve a high CRI above 80 suitable for general illumination. However, Fig. 8.12 visualizes at the same time the drawback of broad emission spectra.
The low energy photons of the red (CGX150) emitter, as well as the high energy photons of the blue (SEB115) emitter do not contribute to the luminance and deteriorate the efficiency. To demonstrate the advantage for device efficiency if a narrower spectrum could be realized, only the part of the spectrum of Fig. 8.12 between 450 nm and 650 nm is used for calculating a theoretical efficiency. It is assumed that the EQE (11.5% @ 1000 cd/m²) of the reference spectrum and the narrowed spectrum are equal. The color coordinates change only slightly from 0.45/0.42 to 0.46/0.44. Impressively, the efficiency would increase by 26%. It is therefore necessary to find emitters which have smaller FWHM emission characteristics or whose emission can be influenced by optical tuning (resonant cavity effects [20]).

Tab. 8.2 summarizes the achieved data of the white light emitting OVPD OLED at a luminance of 5000 cd/m², which would be suitable to be used as light source for general illumination.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>luminance</td>
<td>5000 cd/m²</td>
</tr>
<tr>
<td>lifetime</td>
<td>150 h</td>
</tr>
<tr>
<td>luminous efficacy</td>
<td>18.7 lm/W</td>
</tr>
<tr>
<td>color temperature</td>
<td>2600 K</td>
</tr>
<tr>
<td>CRI</td>
<td>83</td>
</tr>
<tr>
<td>CIEu,y stability (1-10 kcd/m²)</td>
<td>≤0.01</td>
</tr>
</tbody>
</table>

If the achieved data (Tab. 8.2) are compared with the requirements of a light source suitable for general illumination (Tab. 2.2), the white OVPD OLED can fulfill most of them and can compete with white VTE OLED described in chapter 3.6.2. However, the lifetime has to be further improved to meet the requirement of several thousand hours. In conclusion, it is possible to create a competitive highly efficient white OLED by OVPD.
9 Summary and Outlook

The major goal of this work was to develop OVPD-processed white OLED suitable for general illumination. OLED are a part of SSL and a competitor to inorganic LED. While inorganic LED can be found in many consumer products and general lighting applications, OLED are in pre-production facing many basic and technical issues. To avoid falling back in the SSL competition, these issues have to be solved as fast as possible.

Today, the most competitive white OLED are manufactured by established VTE. This work instead focused on OVPD, which is an alternative deposition technology. Due to the utilization of a carrier gas, OVPD is advantageous in terms of deposition rate stability, maximum achievable deposition rate and flexibility to mix organic materials during deposition.

However, it has not been shown that competitive white OLED can be processed by OVPD. This work’s goal was to develop a state-of-the-art white OVPD OLED and to investigate the potential and possible advantages arising from OVPD technology.

Introductory, a short history of artificial illumination and background information were given, followed by an explanation of the physical properties of OLED and different characterization methods. Specifically the importance of photometric values was considered and explained. Measurement setups were developed and software was written to improve experiment throughput and evaluation. Investigations related to the enhancement of the OVPD technology were conducted.

The development of a white OVPD OLED was broken up into key elements which could be investigated and solved separately. First, different procedures to guarantee a long-term stable hole injection at the ITO/organic interface, even at elevated temperatures of 70°C, were presented. Different oxide buffer layers, a p-doped injection layer, as well as the application of a fluorinated organic acid were demonstrated successfully. Concurrently, the p-doping of the hole-transport layer was investigated and the first time single-run deposition of a p-doped OVPD OLED was presented.
Thereafter, a new EL concept termed *cross-fading* was introduced. The concept makes use of the features uniquely offered by OVPD. Due to the system design, it is theoretically possible to mix an unlimited number of organic materials at a continuously variable ratio. A cross-faded EL realizes a broad but confined emission zone, which is stable versus increasing luminance and process variations and flexible in terms of organic layer stack variations. Two-emitter yellow OLED were intensively investigated applying the concept of a cross-faded EL.

Subsequently, the lifetime of monochrome red OLED utilizing different emitters and hole-conducting host materials was investigated in detail. Degradation mechanisms were identified and the concept of *exciton transfer molecules* was introduced. Exciton transfer molecules minimize degradation and helped to increase the lifetime of red OLED dramatically. Afterwards, the concept was successfully transferred to white OLED, to increase their lifetime as well.

Finally, combining all investigations, a hybrid white OVPD OLED was presented and further investigated. The design of the organic layer stack allows easy customization of the color coordinates, which are nevertheless stable with luminance. Achieved efficiencies were compared with calculations and discussed. The increase in efficiency and lifetime of hybrid white OVPD OLED is shown in Tab. 9.1. The goal of an efficient and long-lived white OVPD OLED was realized and the capability of an OVPD system demonstrated.

| Tab. 9.1: Efficiency comparison and achieved data @ 1000 cd/m² of developed hybrid white OVPD OLED. |
|-------------------------------|-------------------|-------------------|
| luminous efficacy [lm/W]      | mid-2008 | mid-2011 |
| (without outcoupling enhancement) |       |       |
| CIE_x/CIE_y                     | blueish-white | 0.45/0.42 |
| CCT                            | NA      | 2871   |
| CRI                            | NA      | 85     |
| lifetime [h]                   | NA      | >1000  |

In future, it would be advantageous to investigate a phosphorescent blue emitter and a fully phosphorescent organic layer stack based on the cross-faded EL concept. Furthermore, it is suggested to investigate alternative hole- and electron-conducting host materials concerning a higher stability against opposite charge carriers.

To further increase the lifetime, different approaches are possible. Preferably, the stacking of complete white OLED can be investigated. The lifetime of a double-stacked
white OLED can be estimated to increase by a factor of 4 if it is driven at the same luminance. To be able to fully stack an OLED in the organic deposition chamber, it could be advantageous to investigate organic n-doping and combine it with p-doping to form a charge generating interlayer. However, presently the instability of available organic n-dopants is a serious challenge without much progress.

In addition, if the light outcoupling could be enhanced, access to a large efficiency increase potential is possible. Regardless of an internal or external outcoupling approach, it is suggested to investigate the possible enhancements due to the use of organic materials (light scattering or layers of different index of refraction).

The concurrent improvement of efficiency, lifetime, luminance and cost of light is the short- and long-term goal for white OLED to be successful in the SSL market.
10 Appendix

10.1 Software

The following software is written in LabView and available as standalone executable packages.

10.1.1 PlotIVL

With a given spectrum and electrical data, PlotIVL is able to perform photometric calculations like true luminous/current efficacy, color coordinates and EQE. Moreover, different spectra can be combined and the resulting efficacies can be calculated.

10.1.2 rQFit

rQFit is a program to manage calibration data necessary for the operation of the AIXTRON Gen1 OVPD system. It stores calibration data in a database, visualizes the evolution of material deposition rates, creates calibration recipes and notifies the user if calibration data is outdated.

10.1.3 RGen

RGen is a recipe generator for the AIXTRON Gen1 OVPD system. With a given organic layer stack, RGen connects to the rQFit calibration database and calculates necessary organic material source flows and deposition times.

In a second step, the calculated data is taken to write a complete script, which can be loaded to the OVPD system to automatically operate and deposit the desired organic layer stack.

10.1.4 GSpec

GSpec is a program to control the USB650 fiber optical spectrometer and connected power supply as well as current meter. It was written to in-situ measure the key data of an OLED after processing in a glovebox environment without the need for an encapsulation. The automatic measurement of several samples is possible without the need for the user to be in front of the control computer.
10.1.5 GLife

GLife was written to comfortably measure the lifetime of OLED. It continuously records, visualizes and extrapolates the photocurrent of an illuminated photodiode as well as monitors the drive voltage of the OLED. Constant current power supplies (steady or pulsed mode) are integrated into the measurement setup to drive the OLED.

10.2 AIXTRON Gen1

10.2.1 Vertical Container Source (VCS)

The main type of source of the employed OVPD system is the vertical container source (VCS) which is based on stainless steel containers (Fig. 10.1 (left)) with a flow-through of carrier gas. The VCS are situated in heated furnaces (source cabinet shown in Fig. 4.8) and 6 different temperatures can be set for 12 sources. The average organic material load is 3 g. The dependence of the deposition rate versus the source temperature is plotted for ETM001 at 500 sccm in Fig. 10.1 (right).

![Fig. 10.1: Vertical Container Source (VCS) (left). Deposition rate of ETM001 at 500 sccm and different source temperatures (right).]

10.2.2 Horizontal Tube Source (HTS)

During this work, a new source module, the horizontal tube source (HTS) (Fig. 10.2 (left)) was attached to the system described in chapter 4.3.3. In the current version, 2 of a maximum of 4 sources are integrated into the system. The sources can be operated at individual source temperatures, but the maximum source temperature difference is 100°C. In contrast to the VCS, HTS are loaded with a maximum of 1 g of
organic material depending on the material density. They are ideally suited to investigate the properties of new materials. Due to the source concept, it is furthermore possible to heat up the sources to evaporation temperature in about 2 h and to cool them down in around 30 min. Therefore, it is also feasible to reduce or avoid the degradation of temperature-sensitive materials.

In Fig. 10.2 (right), HTS temperature versus time is plotted. At 00:00 h the source heating process was started. After 1:30-2:00 h, a constant source temperature can be observed and the source is ready for deposition.

**Fig. 10.2:** Horizontal Tube Source (HTS) (left). HTS temperature versus time (right).

In Fig. 10.3, the deposition rate versus source flow of NPB utilizing a VCS as well as a HTS is plotted. The data points are fitted according to equation (4.6).

**Fig. 10.3:** Deposition rate versus source flow of NPB.
To achieve comparable deposition rates up to a source flow of 150 sccm, it is necessary to increase the temperature of the HTS by 10°C compared to the VCS. Beyond 150 sccm, the deposition rate of the HTS decreases below the deposition rate of the VCS. This can be explained by the mechanical setup of the HTS and a different system geometry factor (compare equation (4.6)).

### 10.2.3 Vacuum Quality

It is of great importance that the least possible amount of oxygen or water diffuses into the OVPD system. Therefore, after any maintenance involving vacuum components, leaks are identified utilizing a He leak detector. The vacuum quality is controlled by the base pressure, which can be reached if the roots-pump main valve is fully opened, as well as the pressure increase rate when the roots-pump main valve is closed. In both cases, the N$_2$ supply valve is closed. In Tab. 10.1, the base pressure as well as the pressure increase rate is given.

<table>
<thead>
<tr>
<th>Tab. 10.1: Pressure values of the AIXTRON Gen1 system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>base pressure</td>
</tr>
<tr>
<td>pressure increase rate</td>
</tr>
</tbody>
</table>

A higher pressure increase rate could not only be the result of an atmospheric leak, but a cooling circuit leak inside the system as well.

### 10.2.4 Substrate Temperature

Inside the deposition chamber, the substrate is placed on a cooled block, which is surrounded by a cooled diffusion barrier. An electrostatic chuck (ESC) is integrated into the cooled block to pull the substrate onto the cooling contact surface of the block. The cooled diffusion barrier is held at a temperature of 20°C, while the temperature of the cooled block can be varied between -10°C to 80°C. All organic material which is not deposited on the substrate sticks to the cooled diffusion barrier. This prevents any material diffusion back in the direction of the substrate.

To evaluate the temperature offset between the substrate and the cooling contact surface, a glass substrate with top-glued thermocouples was transferred into the deposition chamber. At a coolant temperature of 0°C and a showerhead temperature of 350°C, the following substrate temperatures can be measured (Fig. 10.4).
The substrate is cooled not only by the cooling contact surface on which it is positioned, but also by the organic mask which is in contact with the cooled diffusion barrier. Due to the mask cooling influence, the temperature in the middle of the substrate is higher compared to the outside positions. The difference between the highest and lowest measured temperature equals $T_{\text{max-min}}^\text{without ESC} = 5^\circ\text{C}$ and $T_{\text{max-min}}^\text{with ESC} = 3^\circ\text{C}$, while the average temperature equals $T_{\text{average}}^\text{without ESC} = 17^\circ\text{C}$ and $T_{\text{average}}^\text{with ESC} = 15^\circ\text{C}$. Therefore, a good contact to the cooling contact surface can reduce the average temperature as well as the temperature differences.

In Fig. 10.5, the substrate temperature at different deposition chamber pressures with enabled ESC and 0°C cooling contact surface temperature is shown. The average temperature decreases from 19°C to 11°C with increasing pressure (from 0.5 mbar to 1.3 mbar). This is expected due to the better thermal conductivity at higher pressure and an enhanced thermal coupling between the substrate and the cooling contact surface. At 0.9 mbar, a cooling contact surface temperature of 30°C (ESC enabled) and an average substrate temperature of 42°C is measured. Within the investigated temperature range, the substrate is about 12-15°C warmer than the cooling contact surface temperature.
10.2.5 Process Speed

Due to the utilization of a carrier gas, it should be possible to reach high deposition rates at moderate source temperatures. In Tab. 10.2, the deposition rates of important host materials at 500 sccm carrier gas flow and according source temperature are listed. The shown source temperatures guarantee a thermal stability regarding degradation longer than several months.

In comparison, crucibles in a VTE system of comparable size cannot exceed evaporation rates of 0.1 nm/s if the crucible temperature is kept in an acceptable range.

Tab. 10.2: Deposition rates of different host materials at 500 sccm carrier gas flow and at source (VCS) temperature.

<table>
<thead>
<tr>
<th>material</th>
<th>dep. rate [nm/s]</th>
<th>source temp. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>0.27</td>
<td>270.5</td>
</tr>
<tr>
<td>TCTA</td>
<td>0.17</td>
<td>335.8</td>
</tr>
<tr>
<td>TMM004</td>
<td>0.26</td>
<td>300.3</td>
</tr>
<tr>
<td>ETM001</td>
<td>0.63</td>
<td>221.3</td>
</tr>
</tbody>
</table>

For example, before the optimization of the source temperatures, the ETM001 deposition rate was around 0.05 nm/s (comparable to a VTE tool). At a common ETL thickness of 50 nm, the increase in deposition rate decreases the deposition time from 1000 s to 80 s.

In total, the deposition rates allow the processing of a monochrome OLED in less than 10 min while the limiting factor is the metallization chamber. Furthermore, due to the long-term stability of the organic materials at the utilized source temperature, the temperature and thereby the deposition rates could be increased further. However, the maximum organic layer growth speed is limited by the growth mechanism properties as well.

10.2.6 Material Stability

All materials in VCS are kept at a constant evaporation temperature. Therefore, the temperature stability of the organic materials is important and must be considered. Many of the utilized materials have been investigated in [37] regarding their temperature stability. In Fig. 10.6, the calibration data of the newly introduced emitter CGX150 is shown.
After 53 days, the deposition rate at a source flow of 500 sccm has decreased by 24%. A calibration period of 14 days is recommended. The efficiency of red (CGX150) OLED does not change, but if the material source is opened for visual inspection, the color of CGX150 changed. If degraded material was deposited, the efficiency of OLED probably would decrease. Consequently, the degraded material must have a higher deposition temperature and is not evaporated.

### 10.3 Radiometric and Photometric Units

Tab. 10.3 gives a short overview of the units used to quantify radiation either physical or photometrical.

<table>
<thead>
<tr>
<th>radiometry</th>
<th>photometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>radiant power</td>
<td>luminous flux (F)</td>
</tr>
<tr>
<td>[W]</td>
<td>[lm]</td>
</tr>
<tr>
<td>radiant intensity</td>
<td>luminosity (I)</td>
</tr>
<tr>
<td>[W/sr]</td>
<td>[cd or lm/sr]</td>
</tr>
<tr>
<td>radiance</td>
<td>luminance (L)</td>
</tr>
<tr>
<td>[W/(m²sr)]</td>
<td>[cd/m²]</td>
</tr>
<tr>
<td>irradiance</td>
<td>illuminance (E)</td>
</tr>
<tr>
<td>[W/m²]</td>
<td>[lm/m²]</td>
</tr>
</tbody>
</table>
Bibliography


[5] AGL (incandescent, 60 W, 710 lm), EcoClassic (halogen, 42 W, 630 lm), EcoAmbience (CFL, 12 W, 650 lm), MyAmbiance (inorganic LED, 12 W, 806 lm), PHILIPS Datasheet.


[24] G. Wyszecki, and W. Stiles, Color science concepts and methods, quantitative data and formulae., Table 1 (5.5.2) (Wiley, New York, 1982).


[59] OSRAM AG, München, Germany, Product Datasheet.


[79] Philips Research GmbH, Aachen, Germany, LightEX Software.


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