# 1 Introduction

Organic light emitting diodes (OLEDs) have attracted much interest in research and development in the last two decades because of their potential use in displays as self-emitting pixels or backlight solution. They are very thin and therefore lightweight, exhibit low power consumption and can be deposited on different substrates and backplanes allowing for the use in mobile applications. They permit completely new areas of application, not only for displays but also for the field of general lighting, if they are combined with transparent electronics or flexible substrates. This opens up a variety of new design possibilities particularly in ambient lighting. That is why, OLEDs are considered to be the next generation of solid-state lighting, displacing current technologies and shaping the world and its future appearance.

### 1.1 Organic Light Emitting Diodes

The research on light emitting organic semiconductors goes back to Pope *et al.* who first demonstrated the light emission of anthracene crystals [1]. However, high operating voltages were needed for sufficiently high luminance values so that low efficiencies were the consequence. After the development of a novel concept of OLEDs by Tang and VanSlyke a quarter of century later, efficiencies around 1 % were obtained, arousing the interest on the part of display and lighting companies [2]. The revolutionary breakthrough was realized by the introduction of an organic heterostructure allowing for separate transport of holes and electrons into the device. To this day, conventional OLEDs are based on this basic concept comprising at least an organic hole transport layer (HTL) deposited on indium tin oxide (ITO) as the transparent bottom anode, an organic electron transport layer (ETL) and an opaque metallic cathode on top. An additional organic emission layer (EML) is usually sandwiched between the charge transport materials containing dye molecules which allow for light emission in the visible region. In operation, holes and electrons are injected into the device, recombine within the EML and form excitons whose radiative decay leads to the light generation and emission through the ITO coated transparent substrate as schematically shown in Figure 1.1a. In the mean time, further concepts have been established such as the insertion of additional organic layers as exciton and charge carrier blockers localizing the



Figure 1.1: Scheme and working principle of a conventional bottom-emitting (a) single OLED structure and (b) twofold stacked OLED structure with charge generation layer.

emission zone and preventing exciton quenching effects as well as charge carrier imbalance. Particularly, the introduction of phosphorescent emitters led to highly efficient OLEDs with low operating voltages and efficiencies up to 130 lm/W [3,4], underlining their potential use in future display and lighting applications.

However, OLEDs are still lacking long operating lifetimes. One possibility to increase their lifetime, using present organic materials and devices, is to stack a number of OLEDs on top of each other, in order to reduce the current through the light emitting units, while still achieving a given luminance level. This approach is supported by the fact that organic semiconductors provide a large Stokes shift and therefore cause only low intrinsic absorption losses. Moreover, considerations in respect to epitaxial lattice matching as known for inorganic semiconductors do not exist for organic devices. This reduces the cost and complexity of stacking several light emitting units. One has to distinguish between two concepts of stacking. On the one hand, the sub-OLEDs can be separated by a combination of thin transparent electrodes and insulators in order to drive the light emitting units individually. This concept not only allows for longer lifetimes but also for a tunable color emission [5]. On the other hand, the whole stacked device can be driven by only one voltage source when specific charge generation layers are inserted between the light emitting units [6]. Figure 1.1b exemplarily shows the schematic and working principle for a twofold stacked OLED according to the second concept.

### 1.2 Transition Metal Oxides

Transition metal oxides (TMOs) are well known for their fascinating magnetic and electronic properties. For instance, Manganites are found to possess extremely large magnetoresistance and the discovery of high temperature superconductivity in Cuprates in 1986 aroused new scientific interest in TMOs [7,8]. Though the most important transition metals according to these properties are the eight elements with the atomic numbers from 22 to 29, all elements with an incomplete d shell in the periodic table are considered as transition elements. The outer d electrons are thereby responsible for their influence on the metal-oxygen bonding varying from nearly ionic to metallic [7]. In particular, the multitude of preparation techniques and possibilities for the combination of transition metals with other elements of the periodic table leads to a very large quantity of chemical compounds which is comparable to the diversity of organic materials.

Binary transition metal oxides like MoO<sub>3</sub> and WO<sub>3</sub> gained additional attention due to their specific optical properties. Their light absorbing properties change by irradiation or application of an electric field which is known as photochromism and electrochromism, respectively [9,10]. That is why intensive research onto these materials aroused in the early nineteen-sixties which led to the first thin film deposition experiments of TMOs in ultra high vacuum (UHV) systems. Similar to organic small molecules they can be thermally evaporated and can form smooth amorphous films. Moreover, they exhibit high transparencies despite their photochromism. For this reason, TMOs show a high level of technological compatibility with organic materials which led to several combinations in organic devices such as light emitting diodes and solar cells. For example, they are used as buffer layers on top of organic materials, protecting them against the highly energetic particles emerging during the sputter deposition process of transparent conductive oxides [11, 12]. Additionally, they form semitransparent electrodes in multilayer oxide structures [13, 14] and can be used for efficient hole injection either as neat layers or as p-type dopants of organic charge transport materials [15–18]. Finally, thin layers of TMOs have been used as interconnecting units in stacked OLEDs [19, 20]. In any case, they appear to match the electronic properties of organic materials. However, the origin of these properties particularly after their thermal evaporation in UHV is unclear and needs further investigation.

#### 1.3 Goals and Outline

This work deals with the introduction of TMOs in OLEDs as promising inorganic materials, allowing for the effective implementation of device concepts such as hole injection, p-type doping and electric field-assisted charge generation between stacked OLEDs. The focus of the study is on the physical understanding of the TMOs and their impact on the OLED.

Therefore, Chapter 2 starts with the description of the fundamental physics of organic semiconductors and the basics of OLEDs. In Chapter 3, the most important device preparation techniques and analytical methods used in this work are summarized.

Since the electronic properties of the TMOs are the center and pivotal point of this study, Chapter 4 starts with the results of photoelectron spectroscopy and Kelvin probe analysis on thin films of  $MoO_3$  and  $WO_3$ , providing their energy levels and electronic structure. That enables the set up of a new model for hole injection by TMOs, supported by the electronic investigation of the interface dipoles between the participating layers. Additional properties of neat TMO films such as electron blocking and luminescence quenching are discussed at the end of this chapter.

Chapter 5 demonstrates the electrochemical doping of organic semiconductors by  $MoO_3$  and  $Cs_2CO_3$ . First, the impact of p- and n-type doping on the organic ambipolar material CBP is studied by several analytical methods, referring to its electronic, electrical, morphological and optical properties. Then, the determination of the doping-induced charge carrier densities is demonstrated mainly by two measuring techniques, including the Kelvin probe analysis of the thickness-dependent work function characteristics of doped organic semiconductors deposited on ITO, and capacitance-voltage measurements on metal-insulator-semiconductor structures. It is shown that a linear increase of charge carrier densities occurs with higher doping concentrations and that a low doping efficiency of  $MoO_3$  as p-type dopant is existent. The chapter closes with a discussion of the doping efficiency, giving specific and general reasons for this result.

Chapter 6 is dedicated to the charge generation mechanism in interconnecting units between stacked OLEDs. A physical model of the charge generation at doped p-n homojunctions based on CBP is derived by the measurement of thickness-dependent onset voltages of charge injection and charge separation in a specific device structure. In the second part of this chapter, the role of neat TMO films in the interconnecting units is clarified by the measurement of angular-resolved emission characteristics of stacked OLEDs and the analysis of the interfaces between the TMO and its adjacent organic layers. As a result, the actual charge generation is attributed to the interface between the TMO and its neighboring hole transport layer.

Considering the results of Chapter 5 and 6 in respect to the p- and n-type doping of the ambipolar semiconductor CBP, a novel p-i-n homojunction device is presented in Chapter 7 which can be operated both as a light emitting device and a photodiode. Electro-optical

characteristics are demonstrated such as the superlinear increase of the photocurrent with higher optical power densities and the violet light emission. Despite the low external quantum efficiency as a light emitting device, the p-i-n homojunction diode is considered to offer new insights into the physical mechanisms of organic semiconductors.

## 2 Fundamentals of Organic Devices

Organic materials based on conjugated carbon rings can comprise both electrical conductivity and the ability to emit light after optical or electrical excitation. These properties come from their electronic structure which can be explained by considering the organic molecules in aggregated solid-state phase. In the following, the physical fundamentals of organic semiconductors and their implications for the functionality of organic light emitting diodes will be reviewed.

### 2.1 Small Molecules with Conjugated $\pi$ -Systems

Organic semiconductors are based on aromatic compounds of carbon atoms. Normally, a carbon atom exhibits four valence electrons in such an electronic configuration that two of them are in the 2s state and the other two are in the energetically higher-lying 2p states as indicated by Figure 2.1a. Since these valence orbitals are energetically close to each other, bond hybridization can easily occur in order to minimize carbon bond energies. An  $sp^2$  hybridization takes place in aromatic compounds with hexagonal carbon systems as schematically shown in Figure 2.1b. Three valence electrons occupy the  $sp^2$  orbitals taking an angle of 120° to each other and lying in-plane. The remaining fourth valence electron of the carbon atom occupies the  $p_z$  orbital which is orthogonal to the plane of the  $sp^2$ hybrid orbital. Consequently, the carbon atoms are covalently linked in hexagonal rings by the exchange of sp<sup>2</sup> hybrid electrons leading to strong and highly localized  $\sigma$  bonds, while the electrons in the  $p_z$  state only overlap with the other  $p_z$  orbital and form additional conjugated  $\pi$ -bonds. Due to their low binding energy, the  $\pi$ -electrons are delocalized within the hexagonal carbon system and form the extended  $\pi$ -electron system which is responsible for the intramolecular electrical conductivity. The hexagonal carbon system is illustrated in Figure 2.1c. The superposition of the  $p_z$  orbitals results in the splitting of  $p_z$  states into binding  $\pi$ -states and anti-binding  $\pi^*$ -states. The highest occupied  $\pi$ -state of a molecule is denoted as highest occupied molecular orbital (HOMO) and the lowest  $\pi^*$ -state is specified as the lowest unoccupied molecular orbital (LUMO).

While these considerations apply for single isolated organic molecules, the situation changes by condensation to aggregated solid-state phase. Thereby, one has to distinguish between



Figure 2.1: Schematic orbital model of (a) an unhybridized carbon atom, (b) a carbon atom hybridized into the sp<sup>2</sup> configuration, (c) a hexagonal carbon system. (d) Schematic electronic structures of the corresponding orbital models.

small low molecular weight molecules which can be thermally evaporated and long-chain polymers usually deposited by spin coating or ink-jet printing techniques. The main focus of this work is the examination of small molecules, though most of the basic principles also apply for polymers. Due to their closed shell, the organic molecules are only weakly bound to each other by van-der-Waals forces. As a consequence, interactions between  $\pi$ electrons of neighboring molecules are rather low due to the small overlap of their electronic wave functions. Accordingly, the intermolecular electrical conductivity is low and directly associated with a physical transfer of charge carriers from one molecule to the next, leading to ionization effects and resulting in a strong electronic polarization of the neighboring molecules. Depending on the time scale regarding the lifetime of the excited molecule, intramolecular and lattice relaxation add on, leading to geometrical reorganization of directly neighboring and further surrounding molecules in respect to the ionized one. All these effects have an influence on the potential energy of the charge carriers. The electronic polarization, thereby, amounts to 1-1.5 eV, contributing by far the most to the shift of HOMO and LUMO levels towards and against the vacuum level (VL,  $E_{vac}$ ), respectively [21]. Therefore charge carrier transport can be described in terms of polaron transport on HOMO<sup>\*</sup> and LUMO<sup>\*</sup> with a transport gap  $E_t$  which is smaller than the energetic gap between HOMO and LUMO of an isolated molecule. Still, according to the common use in literature, theses transport levels will be denoted as HOMO and LUMO levels, since no further reference to organic molecules in the gas phase will be done in the following. Figure 2.1d summarizes the derivation of the transport levels discussed in this section.

### 2.2 Organic Semiconductors

In the following, the fundamental properties of semiconduction and light emission of organic materials will be explained, including the discription of the charge transport, charge injection, and formation of excitons and the characterization of the energetics at their interfaces. Additionally, the method of electrochemical doping of organic semiconductors will be presented.

#### 2.2.1 Charge Transport

As seen in the former section the charge carriers are strongly localized on single organic molecules due to only weak van-der-Waals forces and a small overlap of the electronic wave functions between the molecular orbitals. Accordingly, their transport levels are narrowed to some 10 meV unlike inorganic semiconductors in which their crystalline structure leads to delocalized charge carriers and energetically broadened conduction and valence bands. The charge carrier transport in organic materials is regarded as a sequence of reduction and oxidation processes between adjacent molecules and can be described by the hopping model [22] which is illustrated in Figure 2.2. The redox process is associated with the formation of cations and anions accompanied by strong polarization and lattice relaxation effects. However, local disorder in amorphous organic materials induces energetic disorder due to a variation of polarization intensities within the bulk material. This effect leads to energetically broadened transport states which are usually modeled as Gaussian distributions [22]. The tail states of the HOMO and LUMO levels are considered to extend into the band gap of the semiconductor and influence the charge carrier mobilities. Charge carriers occupying these trapping sites exhibit a lower hopping probability to overcome the potential barrier to the adjacent molecule. Corresponding to the energetic height of the potential barrier, they need an activation energy  $\Delta W$  which may be provided by the thermal energy kT. The dependence of the mobility on the temperature T and activation energy is given by

$$\mu(T, \Delta W) = \mu_0 \exp\left(-\frac{\Delta W}{kT}\right).$$
(2.1)

The hopping of charge carriers between adjacent transport sites occurs randomly and without a preferential direction for charge transfer unless an external electric field F is applied. According to the Frenkel effect the presence of a strong electric field causes the effective depth of a trap to be reduced in one preferential direction [23], which is also illustrated in Figure 2.2. Thus, the charge carrier mobility is field-dependent and has been found to obey

$$\mu(E) = \mu_0 \exp\left(\frac{\beta\sqrt{F}}{kT}\right),\tag{2.2}$$

with  $\beta$  as the field activation coefficient.

For the description of the general current density versus voltage characteristics (I-V) within



Figure 2.2: Schematic showing thermally activated hopping transport of an electron between Gaussian distributed states of adjacent molecules (with a distance a) assisted by the application of an electric field F.