

OLED Matrix Displays: Technology and Fundamentals

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Abstract

For more than a decade considerable effort has been put into the development of light emitting devices based on evaporated layers of organic semiconductors. To date, the properties of matrix displays consisting of organic light emitting diodes (OLEDs) basically meet automotive and consumer product requirements. OLED matrix displays offer high contrast, wide viewing angle and a broad temperature range at low power consumption. In contrast to polymer devices, OLEDs are processed in ultrahigh vacuum systems. The organic source materials are sublimated from effusion cells. Due to the sensitivity of organic thin films, device structuring by conventional etching techniques is not feasible and alternative structuring techniques were developed. Electrical current in organic devices is

limited by the low conductivity of organic semiconductors and by energy barriers at the metal-organic semiconductor interface. Photoelectric measurements facilitate the determination of barrier height differences between various electrode setups. Further insight in the energy band alignment at organic heterointerfaces are gained by ultraviolet photoelectron spectroscopy (UPS). In addition to widely employed electrical (I-V, C-V) and optical (P-I) measurements, thermally stimulated current (TSC) and luminescence (TSL) allow the characterization and a more detailed understanding of carrier traps and charge transport in organic devices. Energy transfer in a doped OLED emitting layer can be investigated by time-resolved photoluminescence measurements.

1. Introduction

Since the first highly efficient organic light emitting diodes (OLEDs) were demonstrated in 1987 by C.W. Tang and S.A. VanSlyke [1], device technology has continuously been improved. The first commercially available low information content displays based on OLEDs were produced by Pioneer. These early products have already shown that the high contrast of self-emitting displays offers a superior alternative to liquid crystal displays in applications with changing lighting conditions and the need for a wide viewing angle as in the automotive and the steadily growing mobile phone and PDA (personal digital assistant) market. Consequently, on the order of 70 companies worldwide conduct research and development in the OLED field. Display development ranges from low-content monochrome passive-matrix displays to active-matrix full-color displays and SVGA resolution microdisplays.

2. OLED Display Technology

2.1 Organic Molecular Beam Deposition

In contrast to polymer devices, which are fabricated by dipping or spin-on techniques, OLEDs consisting of molecules with low molecular weight are processed in high or ultrahigh vacuum systems. The complete organic molecular beam deposition (OMBD) system is depicted in Figure 1. Following the concepts of inorganic semiconductor MBE systems, it consists of two organic growth chambers (base pressure $\sim 10^{-9}$ mbar), a metallization chamber, a sputter chamber and a substrate pretreatment chamber, connected by a vacuum transfer system. The organic source materials are sublimated from effusion cells. Cell temperatures range from 100 to 450 °C, while growth rates are kept rather low on the order of 2 - 8 nm/min to achieve smooth and homogenous thin films on an ITO-coated glass substrate, which can be cooled. Layer thickness

is monitored with a quartz oscillator. Co-evaporation of organic molecules for doped layers is feasible.

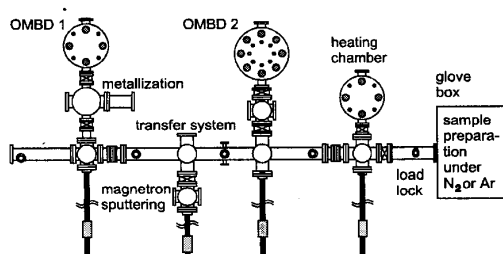


Figure 1: OMBD System.

2.2 In-line OMBD

The conventional OMBD technology is not easily scalable to meet production requirements. It is more promising to follow a different approach. Figure 2 shows an in-line OMBD system, the construction of which is currently in progress. Samples are advanced through the long and narrow vacuum system, which consists of several evaporation chambers. Each of these chambers contains one or two evaporation sources, so that co-evaporation of guest-host systems is possible and a certain flexibility in the layer and material sequence in the OLED production is maintained. The final evaporation process is the contact metallization. For substrate preparation, the OMBD system includes an evaporation chamber equipped with sputter and e-beam sources.

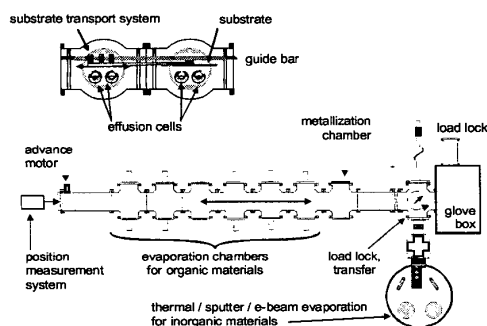


Figure 2: In-line OMBD System.

Advancing a substrate over an evaporation source, which emits a molecular beam through a narrow slit rectangular to the direction of substrate movement, will principally result in a

superior homogeneity of layer thickness. Further, the source material yield is very good. Care has to be taken to avoid organic layer build-up on the sample guiding system. Finally, the processing time per sample for such a system is much lower in comparison to evaporation systems featuring a single (Figure 1) or cluster evaporation chambers. The processing time can further be reduced if a second load lock is implemented at the end of the in-line system or if the system exhibits a "circular" shape, so that the samples return to the starting point after layer deposition.

2.3 Organic Displays

Devices for use in a passive matrix OLED display require a low forward voltage, high luminance efficiency, and a low reverse current. To fulfill these qualifications, OLEDs usually consist of multi-layered structures to facilitate charge injection from the contacts as well as carrier transport into the emitting layer (Figure 4 left). The luminance efficiency can be increased by doping the emitting layer with special dye molecules, e.g. quinacridones [2]. Current-voltage and luminance-current characteristics and a typical device structure are shown in Figure 3.

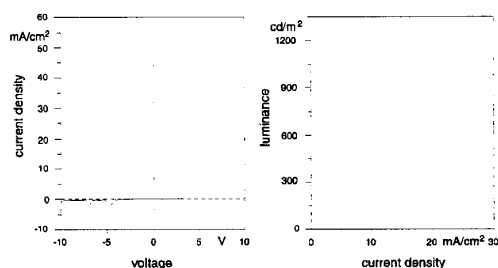


Figure 3: Current density vs. voltage and current density vs. luminance plots for a quinacridone-doped device.

Figure 4 shows a picture of a 100 x 50 pixel monochrome dot-matrix display with a four step grey scale test image. The pixel size

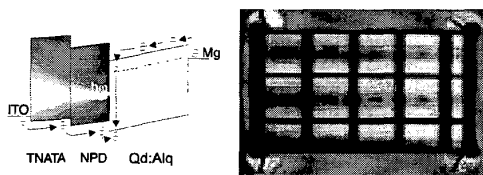


Figure 4: Photograph of a Monochrome OLED Display.

is $270 \times 320 \mu\text{m}^2$ and the gap between the pixels is $30 \mu\text{m}$. In Figure 5 the display is shown inserted in a display mount, which connects the display with the driver electronics. In the passive matrix driving scheme, the devices in one row have a common anode while the devices in one column have a common cathode. A pixel is addressed by driving its respective row and column lines. Crosstalk due to reverse leakage current of neighboring devices can be suppressed by reverse biasing all inactive rows and columns. This is accomplished with the driver electronics in Figure 5, which consist of 100 current sources (16 on each circuit board) to drive the anode currents and 50 open collector drivers (8 on each circuit board) to sink the cathode currents. The driver electronics are controlled by a PC, the display of gray shades is achieved by modulation of the "on" pulse width.

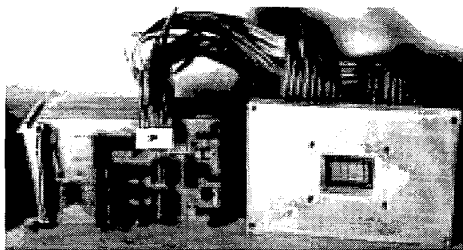


Figure 5: 50*100 Pixel Display with Display Mount and Driver Electronics.

The fabrication process described here is similar to that in [3]. It is based on ITO coated glass substrates. Rows are obtained by etching the lithographically patterned ITO layer. Since the sensitivity of the organic layers to chemicals and humidity does not allow patterning of the metallic top contact after deposition, a different approach has to be used. Due to the desired high

resolution and the resulting small pixel pitch, the adjustment of a shadow mask is to error-prone, especially if one does not want to break the vacuum between organic and metal layer deposition. Instead, we use photoresist barriers to separate adjacent rows. A schematic drawing of the structure is shown in Figure 6. The barriers are 20 times higher than the organic films and metal layer. Furthermore, the photoresist forms a distinct undercut (Figure 7), leading to a reliable separation of the evaporated layers into single columns.

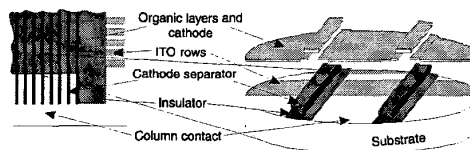


Figure 6: Schematic Structure of the Display.

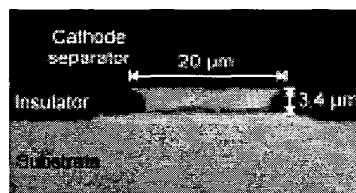


Figure 7: Microscopic Image of a Photoresist Barrier.

3. Fundamentals

3.1 Photoelectric Measurements

Apart from the charge carrier mobility of the organic layers, the contact barriers at the interfaces between metal electrodes and the organic semiconductor and between different organic layers have an important influence on charge transport in an organic device. For the optimization and simulation of a device it is therefore necessary to know the barrier height between the different cathode metals and the organic electron transport layer. The contact barrier does not necessarily depend only on the metal work function and electron affinity of the organic semiconductor as expected according to the *Schottky-Mott* relation [4] (Figure 7) but may additionally be affected by surface states and dipole layers. For that reason it is necessary to

obtain these data from experiments considering the interface formation in the real device.

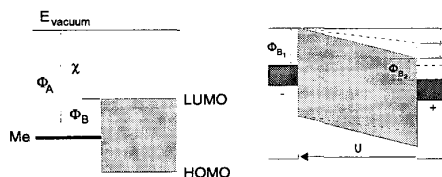


Figure 8: Contact Formation According to Schottky-Mott-relation.

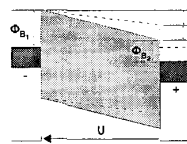


Figure 9: Internal Field Formation as a Result of Built-in Potential Difference and External Voltage.

Using photoelectric measurements it is possible to examine the difference of contact barriers for various metals. The test structure consists of a metal contact on a glass substrate, a vacuum-deposited organic layer, and a metal top electrode. One of the two electrodes has to be semitransparent to allow illumination of the organic layer. A potential difference $\Delta\Phi$ between the barrier heights at the two metal-semiconductor interfaces leads to a built-in field even when the two contacts are shorted (Figure 9). Using an external voltage U the total internal field can be compensated. The generation of charge carriers by illumination of the organic layer with above-energy-gap light is leading to a photocurrent increasing with the total field in the structure.

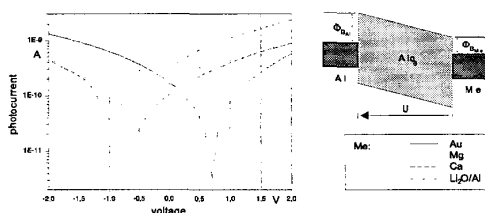


Figure 10: Magnitude of Photocurrent vs. Bias Voltage for an Al/Alq₃/metal Structure.

Figure 10 shows the magnitude of this photocurrent measured by lock-in technique as a function of the applied external bias for different metal combinations. The bias at the minimum of the photocurrent directly corresponds to the difference in barrier heights of the two metal contacts. In Figure 11 the difference between the Fermi energy levels of various metals and

magnesium at an Alq₃-interface is plotted versus the metal work function. For work functions higher than 3.6 eV the *Schottky-Mott* relation appropriately fits the measured levels. For the low-work-function metals like ytterbium and calcium the energy barrier for electrons is higher than expected. This effect has been attributed to surface contaminations leading to a higher work function and image force effects [5].

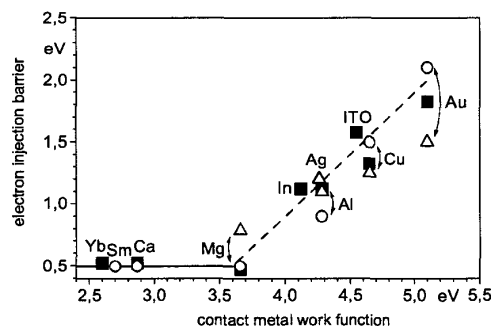


Figure 11: Electron injection barriers determined from photo-electrical barrier height measurements. Dashed line resembles *Schottky-Mott* relation (slope = 1) with a constant barrier offset. For reference, internal photoemission data (O) [6], (Δ) [7] are included.

A similar measurement technique leading to comparable results is internal photoemission. In contrast to the photoelectric technique, one of the contacts, which has to be semitransparent, is illuminated. Depending on illumination wavelength, charge carriers in the contact acquire energy, which eventually suffices to surmount the contact barrier. In principle, internal photoemission yields absolute values for energy barriers.

3.2 UV Photoelectron Spectroscopy (UPS)

In addition to photoelectric measurements, UPS ([8, 9] and references therein) can give detailed insight into the energy level structure at contacts and organic heterointerfaces. The subsequent evaporation and measurement of an organic material allows the investigation of energy level shifts (cf. band bending in inorganic devices) at metal-organic interfaces. Further, contact potentials at organic heterointerfaces, which are inaccessible to

photoelectric measurements, can be determined by UPS. In the following section, we will describe some fundamentals of UPS. UPS examinations of interfaces of common OLED materials with contact metals and organic heterointerfaces will be presented.

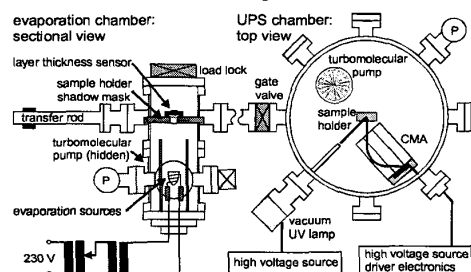


Figure 12: UPS System (Top View) with Evaporation Chamber (Sectional View).

The UPS system is depicted in Figure 12. It consists of a growth chamber equipped with three thermal evaporation sources, from where the samples are transferred to the analysis chamber. A gas discharge lamp operated with helium provides UV light with a photon energy of 21.2 eV. Photoelectrons, which are emitted in direction of the sample surface normal, enter an electron energy analyzer. The described UPS system employs a cylindrical mirror analyzer (CMA) [10], which exhibits an acceptance angle of $\pm 5^\circ$ and a linewidth (HWHM) of 100 - 130 meV. The CMA is positively biased with respect to the sample clearing contact potentials and focusing electrons towards the CMA.

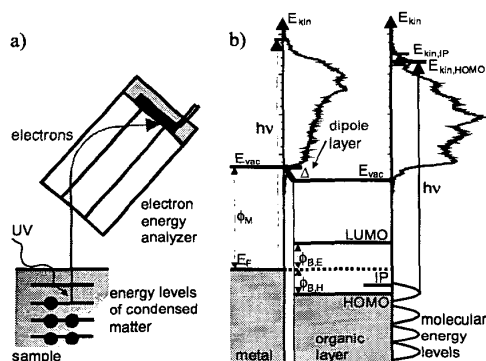


Figure 13: a) Principle of UPS, b) Photoionization and Energy Levels.

Figure 13 a depicts the principle of an UPS measurement. A sample is illuminated with vacuum UV emission (He(I), $h\nu = 21.2$ eV). Photoelectrons, which are emitted in direction of the sample surface normal, enter an electron energy analyzer. Their kinetic energy spectrum is a good approximation of the density of occupied states in the sample. In molecular crystals the density of states can be approximated by the molecular energy levels with a suitable broadening to account for polarization and disorder effects in the solid state. The process of photoemission (Figure 13 b) can be understood by a three step model [11]: (1) Photoionization of a molecule, the photoelectron enters a free electron state of the molecular crystal. (2) Travel to the sample surface (collisions giving rise to the secondary electron background). (3) The photoelectron penetrating the surface and escaping into the vacuum. The difference of photon energy (He(I), 21.2 eV) and electron binding energy accounts for the kinetic electron energy. The secondary electron peak at the low-energy side is a measure of the vacuum level at the sample surface. Typically, a vacuum level shift Δ is measured at metal-organic interfaces [12] which is due to a surface dipole layer.

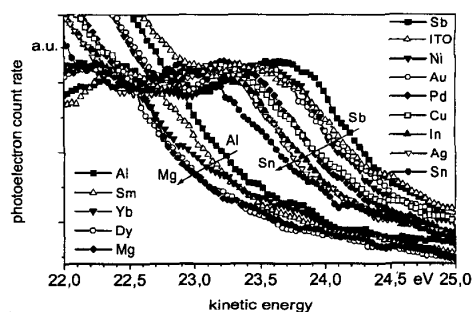


Figure 14: UPS spectra of 4 nm Alq₃ evaporated on vacuum-deposited metal films and on oxygen plasma treated and annealed ITO.

Figure 14 shows UPS spectra of Alq₃ on several contact metals. Determination of the electron injection barrier $\phi_{B,E}$ (Figure 13 b) gives results which are summarized in Figure 15. As the determination of $\phi_{B,E}$ has some uncertainties, most importantly the difference of charge carrier transport states (band gap) and the exact position of the transport state in the UPS peak of the

highest occupied molecular orbital (HOMO), the absolute values of the contact barriers in Figure 15 are somewhat smaller than the results in Figure 11. Nevertheless, an excellent agreement between these results can be observed. Unfortunately, some of the contacts, as $\text{Alq}_3\text{-Sb}$, which would be a good hole injection contact, are unstable under current injection. Although the injection barriers in Figures 11 and 15 generally follow the *Schottky-Mott* rule, barriers of numerous Alq_3 -metal contacts show significant deviations because of interface dipole layers. Therefore, understanding and optimization of OLED injection and transport processes requires the measurement of contact barriers, as these cannot simply be calculated using the *Schottky-Mott* rule with the assumption of a constant vacuum level at the interface.

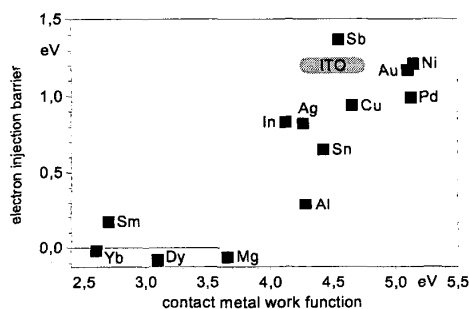


Figure 15: Electron injection barriers determined from spectra of Figure 20. Dashed line resembles *Schottky-Mott* relation (slope = 1) with a constant barrier offset.

Figure 16 shows operating and onset voltages of Alq_3 -TPD OLEDs [11], which qualitatively agree well with the results above. Therefore, it can be concluded that for contact metals with a larger work function than magnesium contact limitation of the device current applies.

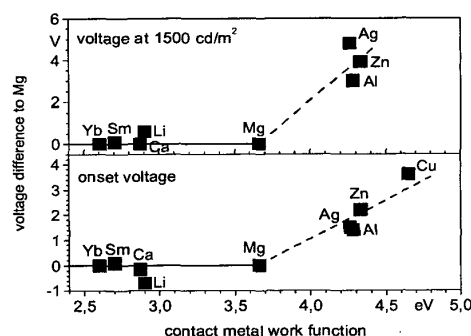


Figure 16: Operating voltage at 1500 cd/m^2 and onset voltage at 0.1 cd/m^2 of Alq_3 -TPD-OLEDs normalized to the corresponding values for devices with Mg cathodes. Lines are intended as guide to the eyes.

Figure 17 shows energy levels from UPS measurements of standard OLED structures with single and double hole transport layers and the respective electro-optical OLED characteristics. The introduction of a second hole transport and injection layer results in a significant reduction of the turn-on voltage while the quantum efficiency is improved. This is attributed to a lowering of the hole injection barrier, which is divided into two smaller steps on the two interfaces. The improved hole injection leads to a more balanced carrier injection which is the reason for a better quantum efficiency.

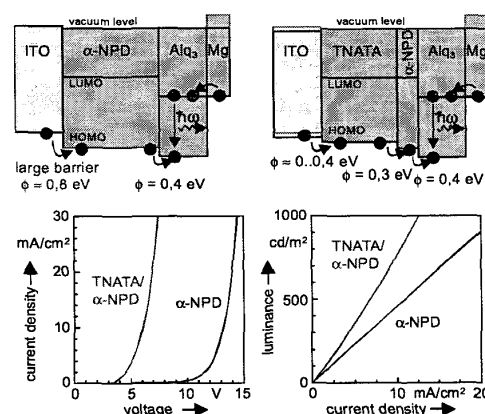


Figure 17: Energy level structures determined by UPS and electro-optical characteristics of OLEDs with single and double hole injection and transport layers.

3.3 Thermally Stimulated Processes

Carrier traps lead to a limitation of the electrical current in an organic layer. Therefore, good conductivity of an organic layer can be attained if the material shows few free traps at room temperature. Traps in organic materials are caused by defects of the organic layer, which can partially be structural defects. As the purity of the organic source materials is rather low compared e.g. to inorganic semiconductors, pollutants additionally are an important source of traps. In this case, a discrete trap level occurs, while statistically distributed structural defects will cause a continuously distributed trap level of a certain energetic width. Finally, the transported charge carriers cause an electron energy level redistribution of the (ionized) organic molecules on which the carriers reside, which can lead to carrier self-trapping. To examine the trap level distribution and trap level density in an organic material, an organic layer is cooled (Figure 18 a) with liquid nitrogen until almost all traps, which are free at room temperature, are filled (Figure 18 b). To achieve unambiguous results contact metals are chosen in a way so that just one sort of charge carrier is injected during the cool-down process. The sample then is warmed up continuously to room temperature, so that the trapped carriers are set free. They cause a thermally stimulated current (TSC, Figure 18 c) with a certain temperature dependence and kinetic. The current exhibits characteristic peaks, which are dependent on the energy and density of the corresponding trap levels. As an example, charge carriers from deep traps are released at higher temperatures. The totally detrapped charge is a measure of the trap density of the material investigated.

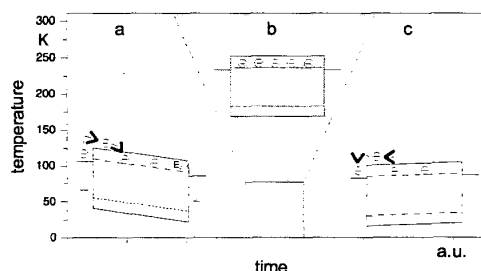


Figure 18: Principle of TSC Measurement.

Figure 19 shows a typical result of a TSC measurement of an Alq₃-layer. Three peaks which belong to different trap levels can clearly be differentiated. The majority of the totally trapped charge is comprised of deep trap levels, which are detrapped in the higher temperature regime. If both carrier types, electrons and holes, are trapped during the cool-down process, the assignment of the thermally stimulated current peaks to electron or hole traps is difficult. The thermally stimulated luminescence (TSL) technique allows to determine at which temperatures *both* carrier types are released in a TSC measurement. If at a certain temperature in the heating process electrons and holes are detrapped simultaneously, they recombine and light emission can be detected.

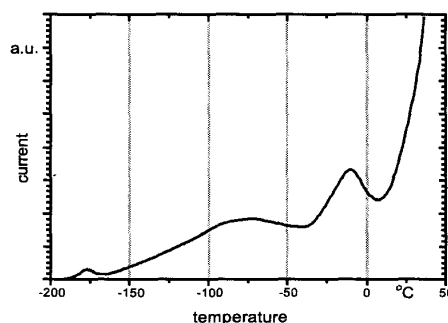


Figure 19: Thermally Stimulated Current Spectrum.

3.4 Dynamics

The dynamic behaviour of OLED luminescence is important in view of optical communications and large flat-panel displays. The molecular excitation in electroluminescence results from the electrical pumping by injection of charge carriers. On the other hand, the molecule can also be photoexcited by absorption of a high energy photon, followed by the creation of an exciton and its radiative relaxation known as photoluminescence. According to this, one can learn about the dynamics of the intrinsic excited state processes by using time-resolved optical spectroscopy. With the help of a femtosecond laser system, it is possible to measure the lifetimes τ of excited states. Thin films of the molecular material are excited by

ultrashort and very intensive UV-laser pulses (approx 100 fs), which may be produced by a mode-locked titanium:sapphire solid state laser and a SHG ("Second Harmonic Generator"). A pulse picker may be useful to reduce the repetition rate so that organic materials with longer luminescence decay times can also be examined.

In the following, the dynamics of energy states are discussed with reference to the guest-host system Ph-Qd:Alq₃ [2]. The pump energy is absorbed by an Alq₃ host molecule. There are two ways of radiative relaxation for the excited state. Either the host molecule decays directly to the ground state, which leads to the luminescence spectrum of pure Alq₃, or the energy is transferred to the Ph-Qd acceptor molecule and Ph-Qd luminescence occurs. The nonradiative transfer of the singlet excited state from a host molecule to a dopant molecule is described by the Dexter-Förster mechanisms in terms of exchange interaction and dipole-dipole coupling, respectively. To optimize energy transfer from host to dopant via the Förster mechanism, a large overlap between the luminescence spectrum of the donor and the extinction spectrum of the acceptor is to be attained. A typical distance for this energy transfer is approx. 5 nm [12, 13], while the Dexter mechanism is much more short-range.

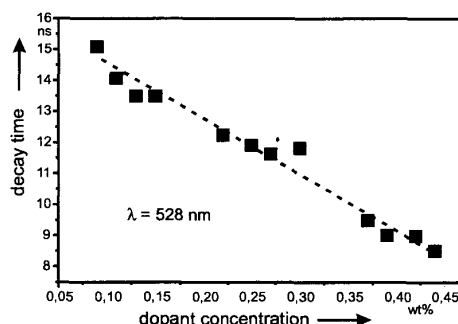


Figure 20: Decay times of time-resolved photoluminescence in dependence of the dopant concentration.

From time-resolved photoluminescence of Ph-Qd:Alq₃ with a dopant concentration of 0.4 wt % a decay time of approx. 9 ns can be determined. By examining thin films with different dopant concentrations, it can be found that the decay time decreases with increasing dopant concentration (Figure 20). This has been confirmed for other guest-host materials, like DCM:Alq₃ [14]. Therefore, it is possible to determine the concentration of optically active dopant in an organic thin film by time-resolved optical spectroscopy. Luminescence decay times generally are sufficiently short for medium to high-resolution display applications.

Acknowledgements

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