Abstract

Self-emissive organic light-emitting diodes (OLEDs) are a new promising technology with high expected profitability on the display market, which is currently dominated by liquid crystals. They show low driving voltages in combination with unrestricted viewing angles, high color-brilliance, light weight, small film-thicknesses and low production costs. Because of the plasticity of the materials they can be deposited on flexible substrates. Nowadays, there are already OLED-display devices available such as PDAs, mp3 players, mobile phones, navigation-systems etc. One can distinguish two material-classes used in OLED: OLEDs based on small molecules, which are deposited by thermal evaporation and the low-cost polymeric OLEDs, which are processed from solution. Initially, it was difficult to realise polymeric multilayer OLEDs, since newly deposited layers dissolved the underlying layers, but are now easily accessible by the use of direct lithography in combination with oxetane-functionalised polymers.

Despite intense research efforts during the last decade there are still improvements to be made in OLED-lifetime and OLED-outcoupling. The light-outcoupling is limited by the refractive indices of the OLED building layers. Simple ray-optics allows to estimate the external quantum efficiency of a standard OLED to 20 % of the initially generated light. 80 %, however, are lost to total internal reflection. To overcome this problem many approaches have been introduced. They can be divided into modifications of the external OLED-architecture (e.g. mesa structures, micro-lenses) and modifications of the internal layer structure. It was demonstrated that diffraction elements, such as periodic structures, are highly suitable to improve light-outcoupling. Doubling of the efficiency and luminescence enhancements up to factors of five were reported with respect to the flat reference devices, but only in combination with very poor overall efficiencies.

Subject of this thesis was to structure well-performing organic OLED-polymers by direct lithography (DL) and investigate their applications in electro-optic devices as diffraction elements. Additionally, photoembossing (PE) should be applied to access structured well-performing oxetane functionalised OLED-materials without any wet-development step. The third method is a combination of direct lithography and photoembossing and is referred to as "combined DL-PE structuring" in this thesis. Further applications of periodic modulated

organic semiconductors, showing amplified spontaneous emission (ASE) while optically excited, are organic lasers.

Firstly, intense studies of the structuring techniques were conducted. The aim was to achieve structures of high modulation (peak to valley distance) in combination with small grating periods Λ ($\Lambda < 400$ µm). The direct lithography of oxetane-functionalized polymeric semiconductors was studied interferometrically as well as by the use of shadow masks. The final structures showed coupled dependencies on intensity, exposure time, initiator concentration, curing, the atmosphere and the underlying layer. Another critical step in direct lithography is the wet development. However, self-structured emitting layers could be successfully tested in OLED applications: strong modifications of the emission characteristics were detected. Since film thicknesses and grating dimensions are on the same scale as the wavelength of the emission, diffractions of higher orders can be observed, which can to be explained by the Raman-Nath-theory. Photoembossing was established, too. Now oxetane-functionalized, well-performing OLED-materials can be structured yielding films with surface- and refractive index modulations. By choice of the cross-linking monomer the resulting refractive index contrasts as well as the final electrical properties of the gratings can be influenced giving the possibility to electro-optical design the photosensitive blend to the desired application. All process-parameters were investigated in detail. Shadow-mask experiments applying a liquid monomer revealed that mass-diffusion is takes place in the millimetre range. Real-time diffraction experiments showed that the diffraction efficiency is a function of the grating modulation as well as the shape of the grating.

All structuring techniques yielded an improvement of the outcoupling efficiency in OLED applications. The improvement factors were typically between 1.2 and 2.0 with respect to the flat reference devices. Even improvements of factors of 1.15 could be detected with respect to conventional OLEDs without additives. In the chosen OLED layer-order emitter-thicknesses between 180-200 nm were necessary to detect maximum diffraction efficiency of the gratings. Parallel polarization of the emission relative to the OLED-grating-fringes was found. Detection of the angle dependent Emission revealed grating influences on the TE-modes as well as on the TM-modes of the gratings. Which mode obtained stronger modification depended on the grating diffraction efficiencies and the dipole-orientations relative to the plane of the substrate. An orientated dipole emits light, which can be diffracted out of the structure and thus be observed outside the device. The polarisation of the emission depends on that orientation. Dipoles orientated parallel to the plane of the substrate mainly contribute to TM-modes, whereas vertically orientated dipoles mainly lead to TE-modes. The diffraction efficiency of a mode is a function of the coupling of that mode to the structure. The dimensions of the grating should match the vertical diffraction conditions for the most lossy wavelength to obtain maximum outcoupling improvement.

By implementation of the periodical structures the device obtains electric modifications, too. At a given applied electric field, the surface relief, i.e. the modulation of the film-thickness, leads to an enhancement of the luminescence in the "valleys" by the E-field improved charge carrier injection. The efficiency improvement of that effect was determined to a factor of 1.058 (5.8%) of the overall maximum improvement (factor of 2), and is therefore considered to be negligible. The effect of the cathode-surface-increase by the relief was also classified to be marginal.

Important electric modifications result from the material re-distributions in the corrugated films by applying photoembossing. Material enrichment is taking place at the peaks, which is followed by a depletion of that material in the valleys. The result is a modulation of the electrical properties, e.g. conductance and mobility, according to the electrical properties of the blend components. In turn, that leads to modulated recombination zones and thus to modified ray optics. A refractive index modulation is also found if the polymers and monomers exhibit different refractive indices, benefiting the outcoupling efficiency of the diffraction-grating. The higher the contrast of the refractive indices the higher is the diffraction efficiency of the structure.

The collectivity of all optical and electrical effects characterizes the external emission of corrugated OLEDs. Theoretical calculations of the Institut für Optik und Feinmechanik (IOF) in Jena confirm these interpretations.

The other application is the implementation of self-structured polymer resonators in organic laser devices. Self-emitting DFB-resonators were fabricated for the first time. By the use of the excellent performing OLED-materials electrically driven organic lasers become more accessible. Two differently structured laser-systems were examined: a photoembossed- and a directly structured system. Both laser-systems exhibited very low optical-excitation thresholds, a crucial requirement for electrical pumping. The photoembossed system could be characterized by its stopband to a mixed gain- and index mode-coupling to the DFB-resonator, thus achieving lowest thresholds of 1.45μJ/cm². The direct-structured lasers are based on pure index-coupling-mechanisms. Here, no stopband could be detected. These lasers exhibit higher excitation thresholds of 5.5 μJ/cm^2. Because of the poor electrical performance of the PS-lasers caused by the addition of a non-conductive low refracting monomer, the system is limited to optical applications. For electrical applications the DS-resonators with their slightly higher threshold are more suitable.

In this thesis, the concept could be realised successfully. It was demonstrated that polymeric materials can be structured, while maintaining the electro-optical properties. Application of the periodic structures leads to outcoupling improvements in OLED-devices and the successful fabrication of conducting organic laser-resonators. Furthermore, advanced knowledge of ray-optics and mode-coupling to grating structures was obtained.

In the near future the implementation of 2-dimensional periodic structures in OLEDs and laser devices is planned. We expect further OLED outcoupling improvements as well as lower lasing-thresholds since more light will be collected and thus diffracted out of the devices.

A significant parameter for the fabrication of corrugated devices by photoembossing and crossed-structuring was the choice of monomer. The monomer properties mainly determined exposure conditions as well as electro-optical properties of the final gratings. Advantageous would be a perfect match of the materials to the desired application and device architecture. Further applications of periodic structures could be their use in organic solar cells to improve incoupling of sunlight into the device. The application is currently under investigation in our group.