Invited Paper

Organic semiconductor devices for micro-optical applications

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ABSTRACT

The use of organic optoelectronic devices such as organic light-emitting diodes and organic photodiodes in micro-optical systems is discussed. Potential applications like optical interconnects and optical sensor systems are examined. Device characteristics including emission spectra, I-V-curves and the dynamic behaviour are analysed. In the combination with a polymeric optical fibre (POF) a transmission line comprising a organic light emitting diode and organic photodiodes is demonstrated. An important step towards integration is realized by coupling the amplified spontaneous emission of an organic semiconductor material into a single-mode polymethylmethacrylate (PMMA) waveguide.

Keywords: OLED, organic photodiode, micro-optics, waveguide, optical interconnect, lab-on-a-chip, PMMA

1. INTRODUCTION

Optoelectronic components based on organic semiconductors are opening new possibilities for a great diversity of systems and applications. There is a wide range of organic semiconductor devices. Light emitters, photodiodes, solar cells, transistors as well as organic lasers have been demonstrated. The versatility of organic components and their application in integrated systems attract much attention for this class of materials.

Organic light-emitting diodes (OLEDs) are already having a significant impact on the display market. Their features, such as low energy consumption, full colours and a wide viewing angle render them ideal for small consumer electronics devices, e.g. MP3-players. Electronic circuits based on organic semiconductors will have a big impact. Radio frequency identification (RFID) tags will be used for low cost electronic tagging. Photodetectors based on organic materials are heavily investigated in the field of photovoltaics. Organic solar cells prepared by low cost processes are expected to bring down the costs for solar electricity. Efficiencies of more than five percent have recently been demonstrated. This progress closes the efficiency gap to amorphous silicon solar cells being on the market.

The integration of organic semiconductors into micro-optical systems has not been in the main focus of research so far. The combination of different organic devices for integrated systems, however, promises completely new products or an improvement of existing systems. The ease of processing and the possibility to deposit these devices basically on any substrate render organic semiconductors attractive for integrated systems in data communication and sensing application.

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2. APPLICATIONS

Here we address two of the basic applications for integrated organic semiconductor devices, namely optical interconnects and lab-on-a-chip devices

2.1 Optical Interconnects

The rapid development of computer and telecommunication systems has led to dramatic improvements in computing power and data transfer rates. One possible solution for forthcoming challenges including higher data transfer rate, transmission distance, reduced cross talk and heat-dissipation are optical interconnects (OI). These systems can be used at several levels of a computer or a communication system like cabinet-to-cabinet, board-to-board and chip-to-chip.
As seen in Fig. 1 optical interconnects are basically the combination of a modulated light source and a photo detector using some kind of optical waveguide in between. The light source can either be modulated actively or can be working in continuous wave (cw) mode using an additional modulator. Waveguiding is realized in planar form as well as in fibre systems. The optical receiver decodes the transmitted signal utilizing a photodetector and subsequent electronics.
Several components of optical interconnects based on organic seminconductors have been investigated recently. Ohmori et al. [1-3] demonstrated both organic light emitting diodes and organic photodiodes (OPDs) on polymeric waveguides for data transfer purposes. Polymeric waveguides and polymer optical fibres (POF) are already used in commercial systems. Electro-optic modulators based on organic materials have reached modulation frequencies in the 100 gigahertz regime [4-6].
A complete system made from organic materials could provide a highly integrated and very cost effective solution for optical interconnects. Organic devices like OLEDs and OPDs can be fabricated on all kind of substrates including silicon, glass and plastics. Direct patterning of organic devices on waveguides would significantly simplify the assembly process, avoiding the most expensive fabrication steps.

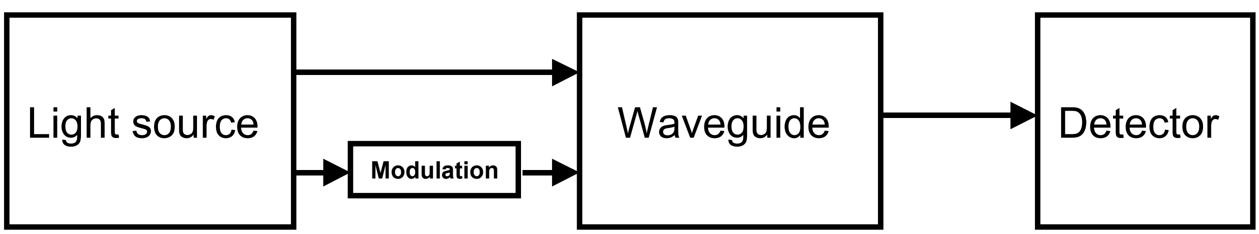

Fig.1: Important parts of an optical interconnect system.

2.2 Optical sensor systems

Sensor systems on the microchip level have gained great interest in recent years. Especially the term “lab-on-a-chip” is commonly used in this context. Devices with “lab-on-a-chip” characteristics are small sensor systems with a high level of integration. Possible applications for such systems are in the areas of medicine, drug discovery and environmental monitoring. There is a clear trend towards decentralization of analytical tasks, i.e. directly at the point-of-care in medical analysis instead of clinical laboratories [7,8].
Optical analysis, such as absorption measurements and laser-induced fluorescence (LIF) are widely used in life science. Figure 2 shows the basic constituents of such a system. A very important part is the excitation source for the analysis. Here, incandescent lamps and various lasers (diode and non-diode) are often used. Recently both inorganic and organic light emitting diodes are employed to minimize both the system size as well as the costs [9-12]. The light is then guided to the analyte by conventional free-space optics or integrated waveguides. The analyte is either placed in a special

detection chamber or in a more complex microfluidic system that provides the transport into the detection chamber. The resulting optical signal is then monitored by the detector. Photomultiplier tubes and semiconductor photodiodes are the most common choice on the detector side.
The use of organic devices in "lab-on-a-chip" platforms promises completely integrated systems containing all necessary components for an analysis. A monolithical integration of OLEDs and OPDs with polymeric waveguides and microfluidic systems on a single substrate would open the way to smaller and cheaper sensor systems. Organic devices can be fabricated on a broad range of substrates including materials often used in microsystems e.g. glass, polydimethylesiloxane (PDMS), polymethylmethacrylate (PMMA) and other plastic materials.

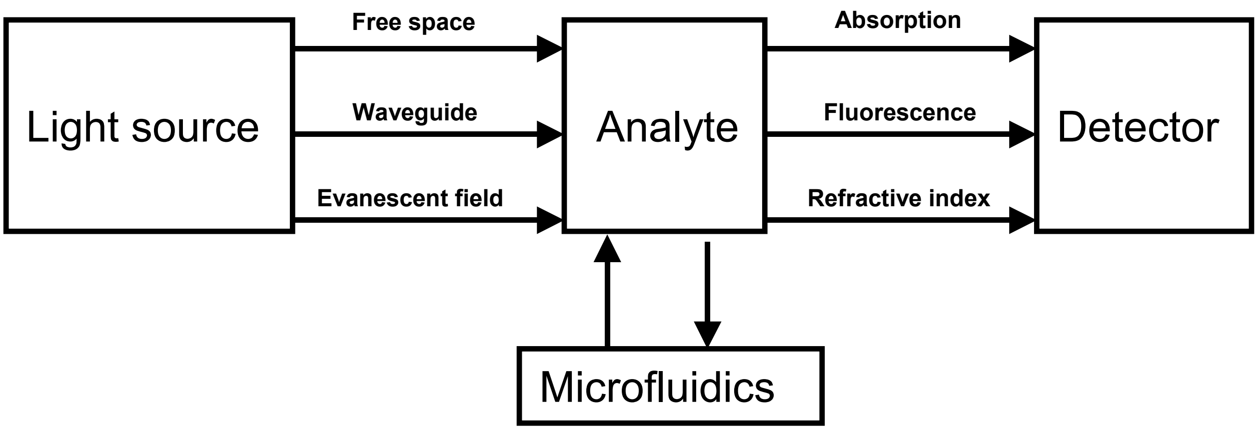

Fig. 2: Parts of an optical sensor system.

3. ORGANIC DEVICES

In the following section the fabrication and characterisation of different organic light emitting diodes as well as organic photodiodes is described.

3.1. OLED materials

Organic semiconductors for OLEDs can be separated into two classes: small molecules and polymer materials. The first class refers to the low molecular weight of the materials. High vacuum thermal evaporation is used for the deposition of these molecules. Polymer materials on the other hand consist of long chains of conjugated monomers. These polymers are dissolved in an organic solvent and processed from solution by wet processing, e.g. spin-coating, doctor-blading or inkjet-printing.
We investigated different materials of both classes for our applications. Processing from solution promises a more cost-effective fabrication whereas vacuum deposition is providing a very controlled deposition of ultrathin organic layers without the use of solvents. One of the goals was to cover a wide range of emission wavelengths by using different emitters for the fabrication of OLEDs.

3.1.1 Fabrication of OLEDs

The OLEDs were fabricated on indium tin oxide (ITO) glass substrates. The ITO substrates were cleaned by ultra-sonication in acetone and isopropyl alcohol and cleaned subsequently in an oxygen plasma chamber. Hole transporting layers were triphenyl diamine (TPD) derivatives for the small molecule devices and poly(3,4-ethylenedioxythiophene)-poly (stryrenesulfonate) (PEDOT:PSS) for the polymer OLEDs, respectively.
High vacuum thermal evaporation was used for deposition of the small molecule materials tris-(8-hydroxyquinoline)-aluminum (Alq_3) (undoped and doped with the laser dye (4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran) (DCM)). The active layers of the polymer OLEDs are a polyfluorene-derivative (poly(9,9-dioctylfluorenyl-2,7-diyl) – end capped with N,N-Bis(4-methylphenyl)-aniline) (Sigma-Aldrich PF6/2am4)) as well as a PPV-derivative (poly[2-methoxy-5(3,7dimethyloctyloxy)-1,4-phenylenvinylen] (Covion PDO 121)). These materials were deposited by spin coating in an inert gas atmosphere. In both cases the cathode materials were thermally evaporated onto the organic layers. In figures 3 and 4 the layer configuration and thicknesses of the devices are shown.

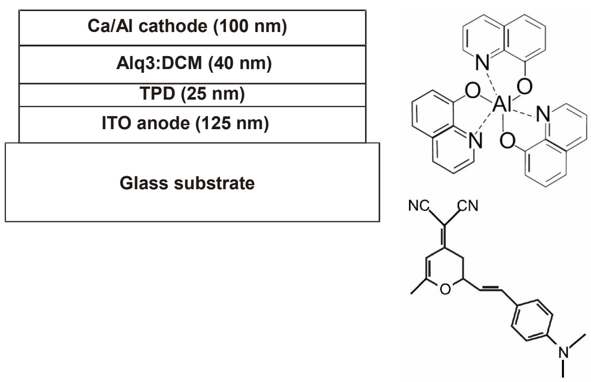

Fig. 3: Alq_3:DCM-OLED scheme and chemical structure of the molecules (top:Alq_3; bottom: DCM).

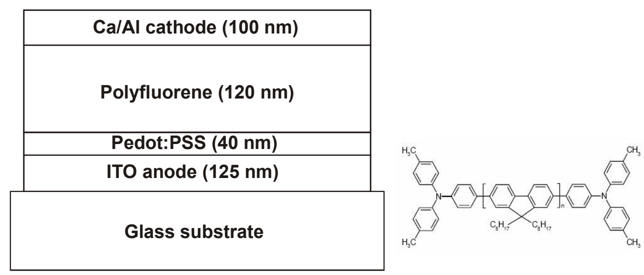

Fig. 4: Polyfluorene-OLED scheme and chemical structure of the polymer.

3.1.2 Characterisation

The devices were tested using a computer controlled characterisation system. This system consists of an automated rotation stage with sample holder, a fibre optic spectrometer (StellarNet EPP2000) and a source measurement unit (Keithley SMU 238). The setup was calibrated using a standard of spectral irradiance (1000 W FEL type) and is providing accurate spectroradiometric and photometric quantities. For sensor applications the total radiant flux (Watts), the radiant exitance (Watts/m²) and the emission spectra of the OLEDs are the most relevant quantities.
The spectral characteristics of the different OLEDs are shown in Fig. 5. All OLEDs show the characteristic broad spectra of organic emitter materials. Similarly to the case of dye lasers the whole visible range can be covered with different materials. As a blue emitter we choose polyfluorene with an emission maximum at approx. 420 nm. The green emitter is undoped Alq_3 that exhibits an emission maximum at a wavelength of 520 nm. For the orange part of the spectrum, OLEDs based on the polymer PDO 121 can be used while a deeper red is generated in devices using the small molecule Alq_3 doped with the laser dye DCM as the emissive guest material.

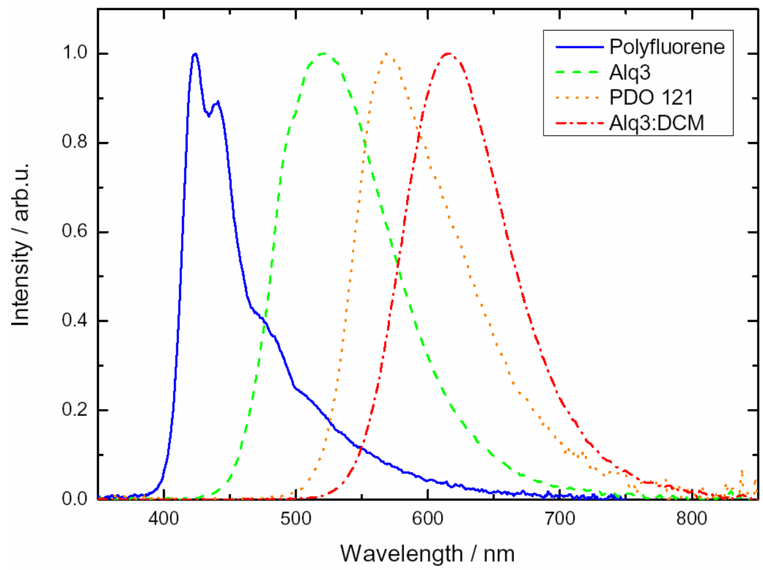

Fig. 5: Electroluminescence spectra of the different OLEDs.

3.1.3 Dynamic response

For the application in optical interconnects as well as in sensor systems the dynamic response of an OLED is of crucial importance. A dynamic characterisation of a polyfluorene OLED has been carried out. The OLED was fabricated as described in section 3.1.1. with a smaller active size (approx. 1 mm²) in order to reduce the capacitance of the device. Patterning of the OLED was realized by depositing an insulating SiO_2 layer through a shadow mask between the ITO anode and the hole transport layer.

The OLED was driven by a signal generator (Wavetek Model 801) with square pulses at different modulation frequencies. The resulting optical signal was detected using a Si-PIN photodiode (Thorlabs DET 210) and monitored by a digital sampling oscilloscope (Welleman Instruments PC scope). Figure 6 depicts the modulation characteristics of the OLED when a 100 kHz square pulse train (Input voltage: 15 V) is applied. By applying a forward bias voltage in the order of the turn-on voltage of the OLED the dynamic response can be improved. In Fig. 7 the modulation of the OLED with an applied bias voltage of 5 V is shown. The OLED follows the modulation frequency up to 300 kHz.

We also analyzed the dynamic behaviour of an Alq_3:DCM-OLED. As shown in figure 8 we could obtain a modulation frequency of up to 1 MHz. The thinner active layers in small-molecule OLEDs are resulting in smaller carrier transit times thus allowing a faster modulation.

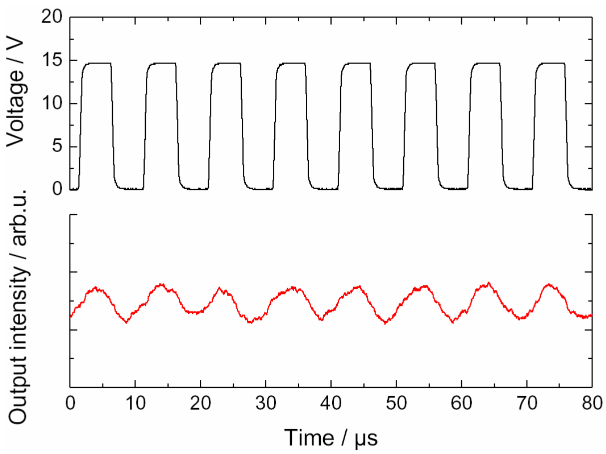

Fig. 6: Modulation of a polyfluorene-OLED with 100 kHz pulses from a signal generator.

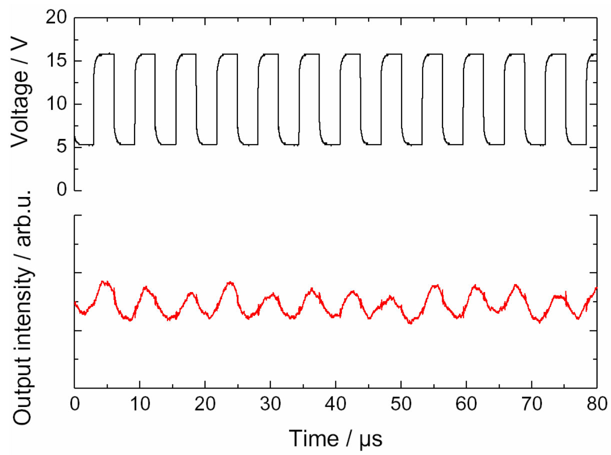

Fig. 7: Modulation of an polyfluorene-OLED with 158 kHz at an applied bias voltage of 5V.

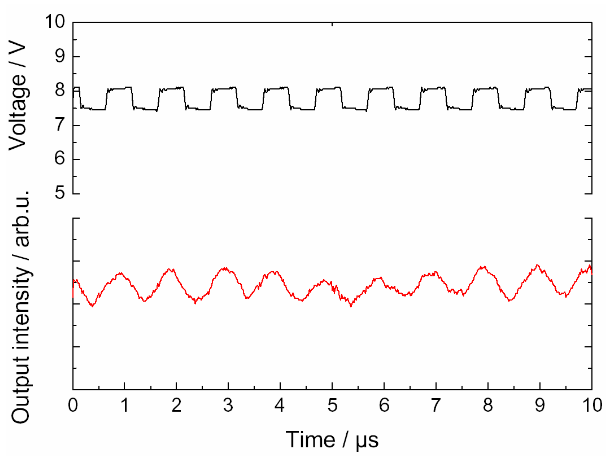

Fig. 8: Modulation of an Alq3:DCM-OLED at 1 MHz (Bias voltage OLED: 7.4 V, Bias voltage Detector: 4.8 V).

3.2. Organic photodiodes

Another important part in optical interconnects and sensor systems is the photodetection. We investigated the composite system made of the conjugated poly-(3-hexylthiophene) (P3HT) and the fullerene derivative [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM) for the use as organic photodetectors.

3.2.1 Fabrication

A scheme of the organic photodiodes is shown in Fig. 9. On top of cleaned glass substrates an ITO anode was deposited by a sputtering process in a commercial deposition system (Leybold Univex 350). The ITO films showed a good transmission rate (more then 85 %) and a sheet resistance in the order of 200 Ohms/Square without an annealing process.
The active size (approx. 1 mm²) of the OPD was again defined by an intermediate layer made from insulating SiO_2 between ITO and the spin-coated hole transport layer (HC Starck PEDOT:PSS). The photon-absorbing layer is a blend of P3HT and PCBM with a weight ratio of 1:0.9. The polymer P3HT acts as an electron donor upon incident light, while the fullerene derivative PCBM is the electron acceptor. This enables an effective charge carrier separation. Finally, an Al electrode (thickness 100 nm) was thermally evaporated onto the organic layer.
The absorption spectrum of the active materials is shown in figure 10. In the visible the absorption is dominated by P3HT.

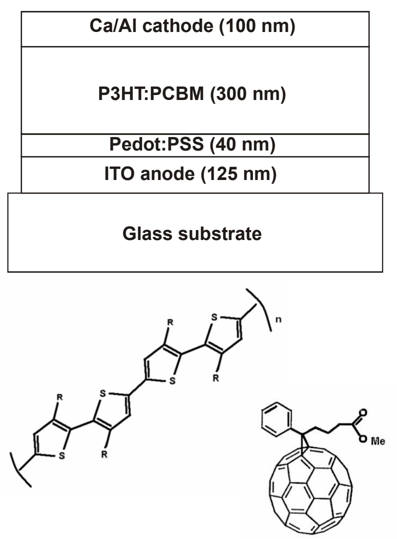

Fig. 9: Device structure of the OPD and chemical structure of the active materials (top: P3HT; bottom: PCBM)

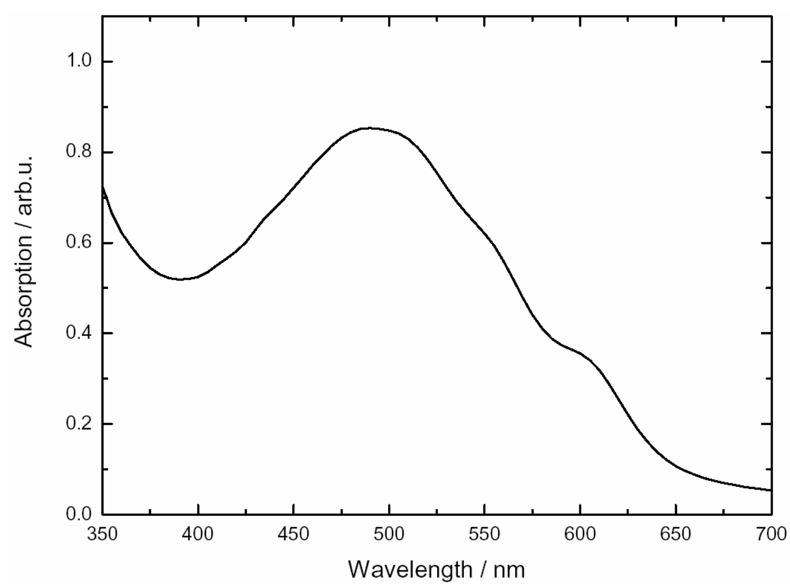

Fig. 10: Absorption spectrum of P3HT:PCBM

3.2.2 Characterisation

For the dynamic characterisation of the OPDs pulsed inorganic LEDs with a peak emission wavelength of 466 nm were used as illumination sources. The LEDs were modulated by a frequency generator (Wavetek Model 801). The dependence of the photoresponse on applied bias voltages was also investigated.
In figure 11 the I-V-characteristics of the OPD in the dark state and under illumination with a simulated solar spectrum are demonstrated. The device shows a very low dark current in the reverse bias region and a good photo-response under illumination.

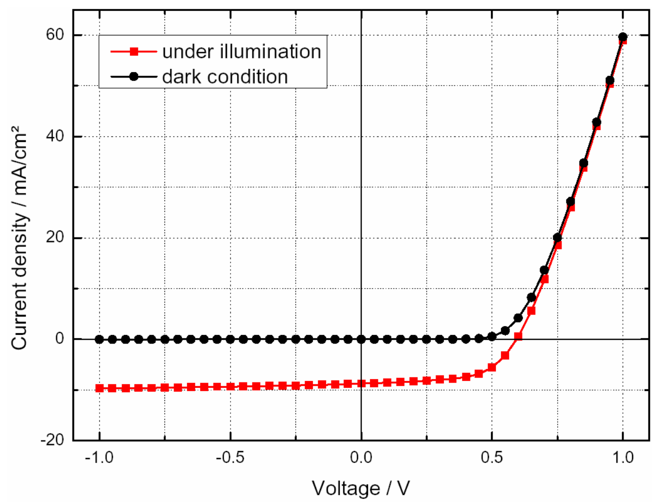

Fig. 11: I-V-characteristics of the OPD in dark condition and under illumination.

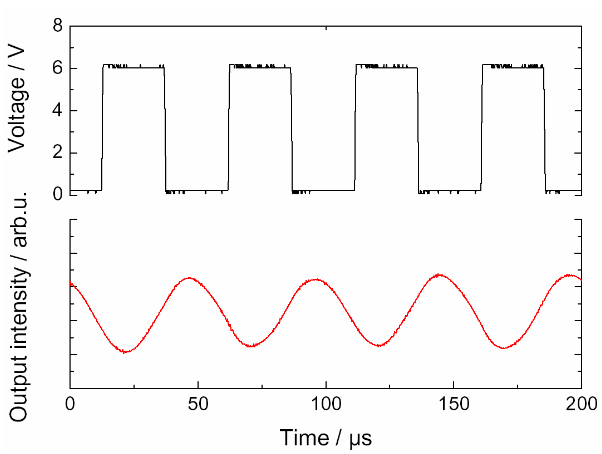

Fig.12: Photoresponse of the OPD under illumination with a blue LED

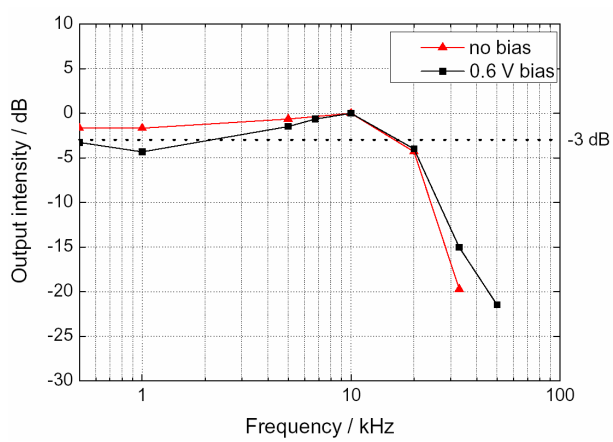

Fig.13: Dependence of the output intensity vs. the illumination frequency and bias voltage

The photoresponse of the OPD under pulsed optical illumination is presented in figure 12. The device shows a good response to the 20 kHz input modulation. The dependence of the photoresponse with different applied bias voltages is shown in figure 13. The device reaches a 3dB cut-off frequency of 17 kHz without an applied bias. A reverse voltage of -0.6 V is improving the response thus enabling the detection of modulated signals of up to 50 kHz.

A further improvement of the dynamic response should be possible with even smaller active areas and hence reduced capacitances. Alternatively, lateral organic photodiodes with extremely short electrode spacing might lead to shorter response times [13].

4. SYSTEMS

The following section will give an overview of realized example systems comprising organic optoelectronic devices. In the first part an optical interconnect consisting of an OLED, a polymeric optical fibre (POF) and an OPD is demonstrated. In the second part the issue of organic semiconductor lasers coupled to waveguides is addressed.

4.1. Optical interconnect

We fabricated an optical interconnect using a polyfluorene OLED and a P3HT:PCBM OPD as described in section 3. Both organic devices were linked via a polymeric optical fibre (core size 0.5 mm). The fibre ends were polished and attached to the glass substrate of the organic devices with a special glue. Figure 14 shows a scheme of the experimental setup. The OLED was driven by a signal generator with an applied voltage of 17.5 V. The resulting photoresponse of the OPD was fed into a transimpedance amplifier and recorded using a digital sampling oscilloscope.
Using this simple passive alignment we were able to transmit a pulse train with a modulation frequency of up to several kHz.

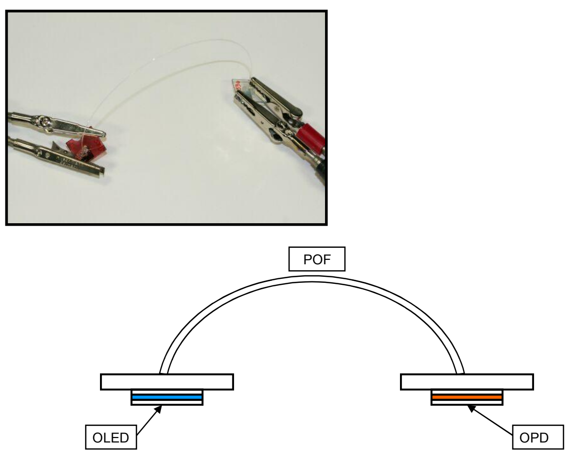

Fig. 14: Image and scheme of the experimental setup for an optical interconnect using only organic active components

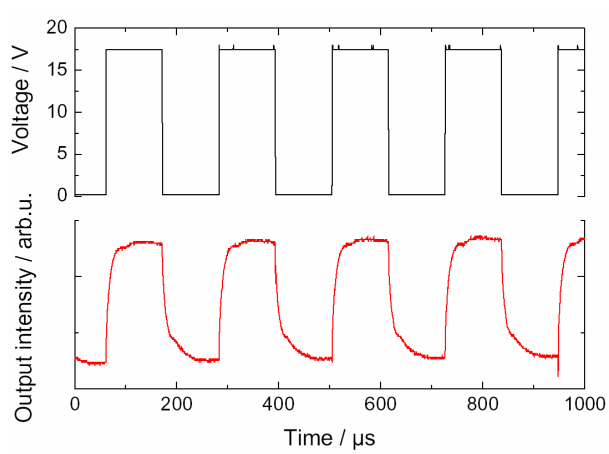

Fig. 15: Response of the OLED-OPD system with an applied input modulation

5. COUPLING OF ORGANIC LASERS TO POLYMERIC WAVEGUIDES

Another class of organic devices has gained much interest in recent years: organic semiconductor lasers [14-19]. The unique properties of such lasers render these devices very interesting for applications like optical sensing. Like OLEDs, organic lasers can cover a wide range of light emission wavelengths spanning from the UV [20, 21] throughout the whole visible range. Even using only one active laser material the tunability can be as high as 50 nm [21]. Up to now only optically pumped organic lasers are realized, but research towards an electrically pumped organic laser is ongoing [22-27].
Organic lasers would be ideally suited for laser induced fluorescence (LIF) applications. The possibility of the integration of such lasers in “lab-on-a-chip” devices would allow to build small, all-integrated devices at very low-cost.
One step on the way to such devices is the coupling of mirrorless lasing (amplified spontaneous emission, ASE) of an organic material into a polymeric waveguide. The following section reports this approach.

5.1 PMMA-based single-mode waveguides

For an all-integrated device we fabricated waveguides based on the material PMMA [28]. This material is commonly used in micro-optics and micro-fluidics. It is transparent in the visible and infrared region, it is biocompatible and it can also be shaped by processes like hot embossing [29]. Another unique feature is the possibility of directly inscribing waveguides through deep ultra-violet (DUV) radiation [30].

5.1.1. DUV induced modification

For deep UV modification, a commercial UV-exposure equipment (Maskaligner EVG 620) is used. A DUV lamp combined with a cold mirror with reflectance in the wavelength range of 200 nm - 240 nm is used in the exposure system. The waveguides are fabricated using vacuum contact at a dosage of 5 J, measured around 240 nm with an intensity meter from Karl Süss. The investigated PMMA type is Hesa-Glas, a homopolymer from Notz Plastics (thickness 500 µm).

5.1.2. Fabrication

Waveguide patterns may be inscribed into polymer films by lithographic techniques using standard photomasks (Cr on glass) or pre-structured polymer plates, as depicted in figure 16. The DUV-irradiation results in a local and controlled increase of the refractive index in the illuminated areas of the polymer surface. This generates the integrated optical waveguide structures in a polymer plate. The refractive index change is up to 0.008 and has a graded index profile with an exponential decay, which reaches a depth of about 5 µm. A typical near field pattern of the facet of such a waveguide is shown in figure 17. A slightly asymmetrical single mode profile is found.

5.1.3. Combination with microfluidics

The waveguides can be integrated into micro-fluidic devices to further enhance the device functionality. In the first step a fluidic channel is realized by hot embossing in a polymer foil. In the next step the waveguides are patterned perpendicular to the fluidic channels by conventional lithography. No further alignment is necessary. In the next step the cover plates were heat sealed onto the hot embossed fluidic channel. The fluidic channel and waveguides were only slightly affected by the thermal bonding process. In the channels, an aqueous dye solution (water mixed with methyl orange) shows a fast and steady capillary flow and no leakage into the welding zone. The use of flow cells with dimensions near the typical length of subjects to be analyzed might be a suitable technique to use for the monitoring of specific reactions of functional beads in fluidic microstructures.

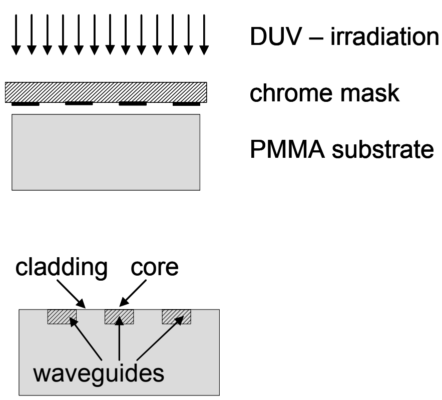

Fig. 16: Fabrication of buried single-mode waveguides in PMMA.

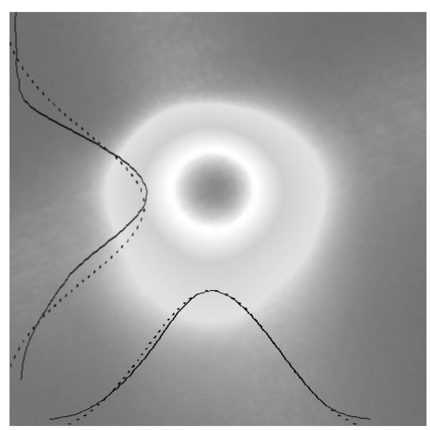

Fig. 17: Near field photo of waveguide facets and guided mode profile compared with gaussian profile.

5.2 Amplified spontaneous emission coupled into PMMA waveguides

For the coupling experiment we deposited a patch of the organic laser material Alq_3:DCM (thickness 350 nm) onto a PMMA substrate with integrated waveguides (width 10 µm) in a thermal evaporation process under high vacuum conditions. The organic material has a refractive index of approximately 1.76 thus building a slab waveguide on the PMMA substrate (n=1.5). The material is then optically pumped with a short-pulse UV-laser (Crystal laser FTSS 355-Q; wavelength 355 nm) under inert gas atmosphere (see Fig. 19 for a scheme). At high enough pump intensities the gain in the active material exceeds the losses and spontaneously emitted photons are amplified in the waveguide. A collapse of the emission spectrum is observed, since only those photons are amplified whose energy coincides with the spectral position of the maximum material gain. Figure 18 shows the resulting gain narrowing. Even without a resonator structure the resulting emission spectra of the Alq_3:DCM material is spectrally narrowed. This might be an interesting alternative for semiconductor laser and LED excitation of fluorescence marker molecules.
The amplified spontaneous emission in the Alq_3:DCM patch on the PMMA substrate is coupled into the waveguide via the evanescent field. The measured mode profile of the emission in such a waveguide is displayed in figure 20.

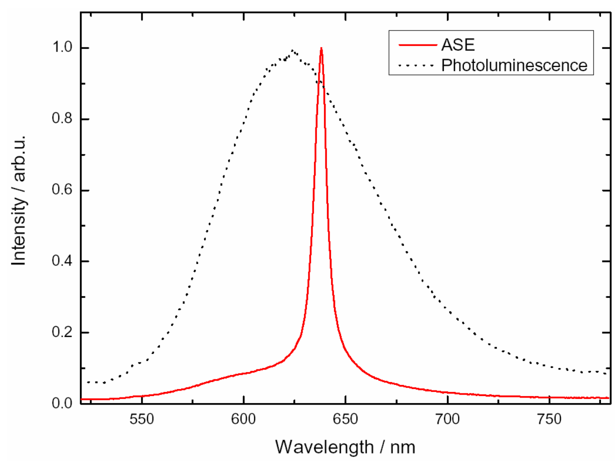

Fig. 18: ASE in Alq_3:DCM layers (ca.100µJ/cm²)

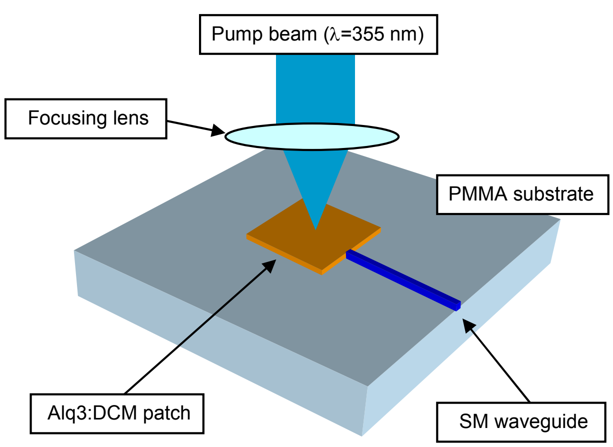

Fig. 19: Scheme of the experimental setup.

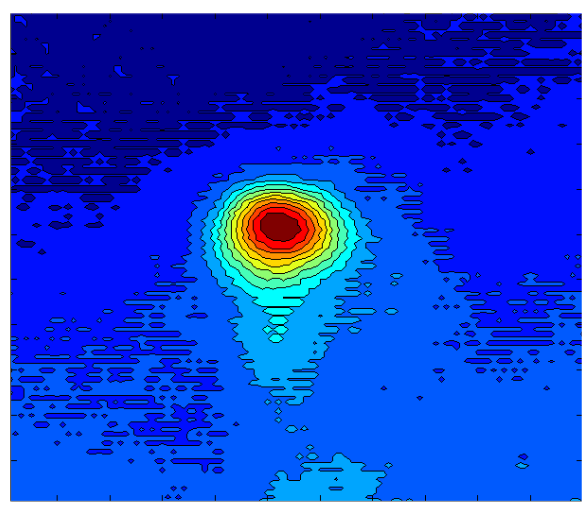

Fig. 20: Mode profile of the ASE output from the PMMA waveguide (5x5µm²).

6. CONCLUSIONS AND OUTLOOK

We demonstrated the feasibility of integrating organic devices in different micro-optical systems. Their use as cost-effective devices in optical interconnects and sensor systems was analyzed and some examples were discussed. A data transfer rate of several kHz in the optical fibre link was accomplished. "Lab-on-a-ship" devices will produce an increasingly commercial interest in the near future. The development of novel, cheap and eventually disposable integrated optical sensors for environmental, chemical and biological monitoring utilizing organic devices and materials will have a great impact. OLEDs and OPDs for fluorescence marker detection and the combination of organic lasers and polymeric waveguides are currently investigated.

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