Abstract PhD-thesis

'Characterization of photorefractive polymer-composites for real-time NIR applications',

by Sebastian Köber, University of Cologne 2012

# Abstract

This thesis focusses on the optimization of organic photorefractive polymer composites for real-time applications in the near infrared. Photorefractivity denotes the light-induced modulation of the refractive index of a material in response to illumination with an interference pattern. This is equivalent to the recording of a phase-hologram. Since the photorefractive effect is based on photoconductivity and electro-optic effects concurrently present in the material, the induced changes of the refractive index are inherently reversible.

Holography requires the superposition of two mutually coherent light beams in order to form an interference pattern. Thus, the photorefractive material may act as a filter to discriminate coherent from non-coherent photons. This forms the basis of the Holographic Optical Coherence Imaging (HOCI) technique, which is capable of depth-resolved imaging of biological specimens like dermal skin or the cornea of the eye. This technique requires high-performance photorefractive systems, which is especially true for *in vivo* applications.

Technically, high performance is specified by a high material sensitivity, which denotes the formation of a high diffraction efficiency hologram with a fast dynamic response. The sensitivity of the materials is characterized by holographic wave-mixing techniques. In some cases, results on photo-electric parameters are discussed to deduce trends obtained by the holographic measurements.

The photorefractive composite materials in this work are guest-host systems comprised of a hole-conducting polymer film, which is doped with electro-optic chromophores and and a small amount of sensitizers for charge generation. In this thesis, each component is subject to independent optimizations with regard to the sensitivity of the composite.

Composites based on newly designed hole-conductors based on triarylamines are fabricated and compared to a literature-known blend based on a carbazole polymer. The significantly enhanced sensitivity of the materials (factor 5 and factor 3 for two triarylamine materials) is further increased by adjusting the sensitizer content. Composites with 15 wt.% sensitizer feature up to a factor 5 increased sensitivity compared to the respective reference material with 1 wt.% sensitizer.

Photorefractive polymer composites demonstrated in literature so far are exclusively p-type materials. The sensitizers used in this work are fullerene-derivatives and hence electron acceptors, which leads to n-type behavior at high sensitizer concentrations. The implementation of a novel mixture of fullerene derivatives made possible to fabricate a material series showing a transition from predominantly p-type to predominantly n-type composite materials through changes of composition. Proof of the change in majority charge carrier is provided by holographic and photo-electric measurements.

The partial exchange of the incorporated chromophores for specifically designed high-performance dyes based on merocyanines did not lead to any significant ma-

terial improvements, due to the low solubility of the dipolar molecules in the apolar triarylamine-based polymers.

Subsequent optimizations in this work elaborate on the influence of the sensitizer-molecule on the sensitivity of the composites. Increasing the acceptor strength of the sensitizer is shown to be an effective approach, the reduction of the recombination rate between oppositely charged carriers is identified as reason for a five-fold improvement of sensitivity within a series of fullerene derivatives. Similarly, adjusting the bulk absorption of the composite by reducing the band-gap of the sensitizer by chemical modifications introduced an enhancement of sensitivity by two orders of magnitude. The introduction of a non-absorbing electron-acceptor, however, is found to reduce the field-requirements necessary for optimum diffractive properties of the materials. A higher fullerene derivative is furthermore demonstrated to be highly sensitive at longer wavelength, which is a prerequisite for opthalmic imaging applications by the HOCI-technique.

The differences of the sensitivities obtained for the materials are further verified by write-erase cycles under video-rate conditions. Moreover, the reference material is shown to be capable of performing 7 million subsequent write-erase cycles under typical measurement conditions. A demonstration of the imaging performance of the optimized composites described in this work is given by depth-resolved imaging of an *in vitro* rat tumor spheroid.

First steps towards the implementation of photorefractive composite materials in integrated photonic devices are undertaken by controlling wave-guided light in a thin photorefractive polymer slab.