Abstract

Together with applications in organic light emitting devices and solar cells, one of the most exciting applications for functional polymers is in holography and holographic data storage. Within the group of photoactive materials, photorefractive (PR) polymers, on the one hand, are considered as a very promising candidate for reversible holographic applications, and photoanisotropic systems (like organic-inorganic hybrid sol-gel materials), on the other hand also exhibit a great potential for use in holographic storage. This thesis focuses on experimental as much as theoretical work on both types of materials, PR polymers and azo-functionalized sol-gel materials, and compares their performances. (**Part A**) Since the discovery of photorefractivity in a polymer in 1991, impressive advances were made in terms of efficiency, sensitivity and stability of organic PR polymeric systems, in which the improvement of the performance was the result of rather empirical approaches. However, better performance is still required to match the requirements of most real world applications, and a deeper understanding of the PR mechanisms in polymers is desirable. In this thesis, investigations of the general PR features were carried out using a system similar to the first reported highly efficient organic PR material. The system consists of a chromophore-doped poly(N-vinyl) carbazole (PVK) matrix, sensitized to operate at red-NIR wavelengths. This material provides a rather well-known system exhibiting large PR response and, due to its low glass-transition temperature, *orientational enhancement*, which is, in most cases, a prerequisite for high performance. (**A.1**) The PR performance strongly depends on the recording geometry through a number of intercorrelated features. On the one hand, this offers an interesting way to improve the sensitivity of the devices, and on the other hand, it allows to gain new insights into fundamental aspects of photorefractivity in polymers or into the properties of the material. The systematic variation of the recording geometry in a transmission configuration led to an optimized geometry, in which both the refractive index modulation and the sensitivity exhibited a significant enhancement with respect to the commonly used standard geometry (by a factor of 5 and 15, respectively). In order to gain a physical understanding of the important dependencies involved the underlying theoretical models had to be reformulated. It

was found that writing the fundamental dependencies in terms of the grating tilt and grating spacing, helped in gaining a better intuitive understanding of the processes. The agreement between experiments and theory was, in general, very good, even with respect to the grating response time, which was less investigated so far. Unexpectedly, a marked increase of the steady-state space-charge field was observed with increasing grating spacings. Reduced recombination rates or the influence of higher spatial orders of the space-charge field were proposed as a plausible explanation. Among other aspects, the systematic analysis of the experimental data allowed to determine the dependence of the trap density in the material on the applied field. The theoretical analysis allows to predict the optimal recording geometry for a given system. Thus, in the material investigated, a further improvement of the sensitivity by a factor of 2 (with respect to the best of the geometries used in this work) is expected to be achieved in an ideal recording geometry. (**A.2**) Reflection-type configurations were also extensively investigated. Reflection gratings exhibit some fundamental advantages, rendering them interesting for example in the field of telecommunications. However, performances reported to date in the literature were always much inferior to that in transmission geometries. This might explain why these types of holograms were rather unexplored so far. This work started by analyzing the expressions derived from Kogelnik's coupled wave theory for reflection gratings. This allowed us to explicitly show the fundamental advantages of these types of holograms. Among others, absorption losses are intrinsically lower compared to the transmission case, which results in fundamentally higher *external* diffraction efficiencies (theoretically, 100 %). In this thesis, the highest performance ever observed in a PR polymer using a reflection configuration was obtained. The performance was comparable to transmission holograms (similar sensitivities were obtained). Moreover, the optical gain and the grating build up speed clearly exceeded those achieved in standard transmission geometries (by factors of 3 and 5, respectively). The analysis of the theoretical description confirmed that such a high performance is possible in spite of the low saturation field. Moreover, it was shown that both electro-optic and birefringent contributions to the refractive index modulation mutually compete, even for p-polarized readout. The low electro-optic coefficient of the material investigated favored the large effect obtained. The basic features of reflection gratings were studied. The dynamics exhibited an oscillatory behavior, which is probably related to the temporal evolution of the space-charge field, although further verification is required. Finally, the investigations on the influence of the recording geometry showed discrepancies with the theoretical predictions. These differences were explained by the field-induced anisotropy of the material, which is typically not considered in the theoretical analysis. (**A.3**) The development of new experimental techniques for easier and more complete material characterization is an integral part of the general strategy for material improvement. A novel technique for holographic characterization based on simple ellipsometry was proposed in this thesis. Such a technique is of interest since ellipsometry is easy to adjust and rather insensitive to grating bending compared to the standard grating characterization by means of diffraction efficiency measurements. The new method uses the influence of the generated space-charge field on the ellipsometric signal. It was demonstrated that the changes on the ellipsometric transmission reproduces the diffraction efficiency for a number of recording conditions. A model was developed to describe such influences, which allowed the calculation of the space-charge field directly from a single ellipsometric measurement. The agreement with the results obtained from moving-grating experiments verified the validity of this model. A great advantage of this model is that no further assumptions are necessary for the calculation of the space-charge field, which allows for direct comparison between the experimental results and the existing theoretical models. The use of a compensator greatly enhanced the sensitivity of the experiment and enabled the measurement of the space-charge field at low external fields (down to 0.5 V/µm), i.e. in a region, where standard wave-mixing experiments are generally not reliable (typically, down to 10 V/µm only). (**Part B**) Besides PR materials, other photoactive systems like photoanisotropic materials exhibit interesting holographic features, even without the necessity of an external electric field. In the past ten years, promising azo-containing hybrid sol-gel materials exhibiting photorefractivity were proposed. However, their performance qualitatively differed from PR polymers and the contribution of the anisotropy gratings probably present in the material were not yet investigated. The last part of this work was dedicated to the comprehensive examination of a novel non-photorefractive centrosymmetric sol-gel material, in which holograms were recorded by photoisomerization of the chromophores. This enabled the exploration of the potential of photoinduced anisotropy gratings for high-performance holography. Highly efficient gratings were recorded in the absence of an external field. Surprisingly, very high gains were obtained (up to 900 cm^{-1}), which implies a nonlocal nature of the grating, in spite of the absence of charge generation or transport processes. The occurrence of a phase shift was verified by moving-grating experiments. This is the first report on phase-shifted photoinduced anisotropy gratings. The gratings recorded exhibited very interesting new features, like the possibility to modulate both diffraction efficiency and phase shift solely by changing the write beam intensity ratio. The behavior of the phase shift, which in general strongly differed from common PR materials, was investigated under different recording conditions and geometries. A semi-empirical model was developed to explain the novel recording operation. In this model, both the amplitude and the phase shift of the photoinduced anisotropy grating are assumed to be directly proportional to the total Poynting vector. The predicted dependence on 1) the intensity ratio, 2) the recording intensity and 3) the grating tilt was in excellent agreement with the measurements. As one application of this model, the control of the optical gain by an external light source was demonstrated (*gain steering*). The unique properties discovered promise interesting perspectives for future applications. In summary, the investigations of a standard PR polymer not only provided new insights into fundamental aspects of the photorefractivity in this type of materials, but also led to a significant improvement of the performance. Studying a novel sol-gel material, a new way for nonlocal recording of holograms without an external field was found. This opens a possibility to extend the applications based on the occurrence of optical gain to non-photorefractive media. In conclusion, two very different approaches to efficient photoactive media were investigated, where the PR polymer exhibits clearly the faster response times, but relative high electric fields are needed. In contrast, the sol-gel material requires no external field and shows stronger two-beam coupling. Note, however, that reflection gratings in the sol-gel material exhibited response times comparable to that of transmission holograms in the PR polymer at moderate fields. Moreover, long dark decay times were observed in the sol-gel material, which would enable long-term holographic storage. The results obtained in this work should contribute to the search for suitable media for holographic data storage.