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Polymer holography I – Method and experiment

Polymerization and networking as a method of permanent holographic record formation

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Summary

Processes of radical photopolymerization running during the holographic exposition in photopolymer recording materials are investigated. Special experimental setup, which makes recording and continuous measuring of the forming hologram possible, was built up. An acrylamide-based recording material was prepared and tested. Our experiments verified that addition of bis-acrylamide improves the stability of the hologram due to micronetwork formation.

Introduction

Optical holography is a method [1-2] of storing and reading full optical information which includes both phase and amplitude of the electromagnetic wave. All types of recording materials are essentially quadratic detectors and hence they are capable of recording just the square modulus of the amplitude and the phase information is lost. However, the phase is not lost when the signal wave interferes with the reference wave (usually a simple plane or spherical wave); the phase is then converted into a spatially modulated amplitude of the standing wave the square of which can be recorded. The phase hologram is a quasiperiodical structure with similar spatial distribution of the refractive index as the recording interference field. When the hologram is illuminated with the reference wave, the original signal wave is revealed due to diffraction on a hologram quasi periodical structure. The holograms (diffractive structures) are typically used in such applications as diffractive optical elements, head-up displays, holographic interferometry, or holographic memories.
The process of light-induced radical polymerization is used in mechanisms of holographic record formation in photopolymer recording materials (e.g. [3-4]).

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Photopolymers differ from conventional recording materials (silver-halide emulsions and dichromated gelatine) in their self-developing characteristics. The detectable hologram is formed already during the exposition procedure and so no additional wet chemical developing process is needed. Therefore we can detect immediately the formation of the hologram and thus also the polymerization process itself. Clearly, the refractive index modulation must be stable. Hence, to obtain a stable hologram it seems that addition of crosslinker is necessary.

Experimental

Recording mechanism

The recording mechanism, which runs during exposition and leads to the local changes of refractive index in the recording material, is described as follows. Light (interference field) induces radical polymerization of monomer. The polymerization rate in darker places of the interference field is slower than in the bright ones and hence a concentration gradient of monomer arises. The monomers diffuses from dark to bright places where it polymerizes. The process results in spatial-modulated polymer concentration and therefore also in the spatial-modulated refractive index. The diffusion of monomers towards the bright regions is schematically visualized in Figure 1. Two plane waves E_1 and E_2 interfere and form harmonic periodical distribution of intensity I(x). Recording process of the harmonic interference field is described by the diffusion model [5-10]. It is based on the diffusion and polymerization equation for monomer molecules. Solutions of the model give good prediction on the influence of the overall intensity or rather the ratio of intensities, but it cannot satisfactorily explain either the behavior of a material in the initiation stage or dependence on the period of the interference field. A hologram recorded with the help of such harmonic field is called a phase diffraction grating and is used for testing material responses.

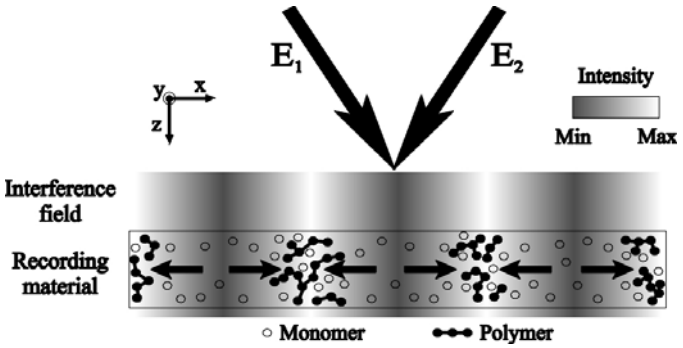

Figure 1. Scheme of the recording process in the photopolymer recording material.

Measuring setup and detection method

To measure the behavior of the material during the recording process we have built a measuring setup which makes it possible to perform recording and simultaneously detection of the growing grating in situ. The setup on holographic table for this experiment is given in Figure 2. Light from cw SHG Nd:YAG laser (532 nm) is split into two beams and directed with mirrors, on the recording material where the beams

overlap. For simplicity, we use two spherical waves formed by spatial filters, which make a harmonic interference field as the two plane waves would, with spatial period 695 nm (incident angle of both waves is 22.5°). To detect the forming structure of the transmission grating, the material is illuminated with the collimated laser diode beam of a different wavelength (656 nm). The red beam is adjusted at the angle 28.1° which fulfils the Bragg condition for the maximum of diffracted intensity. The intensity time evolution is then continuously measured by the detector.

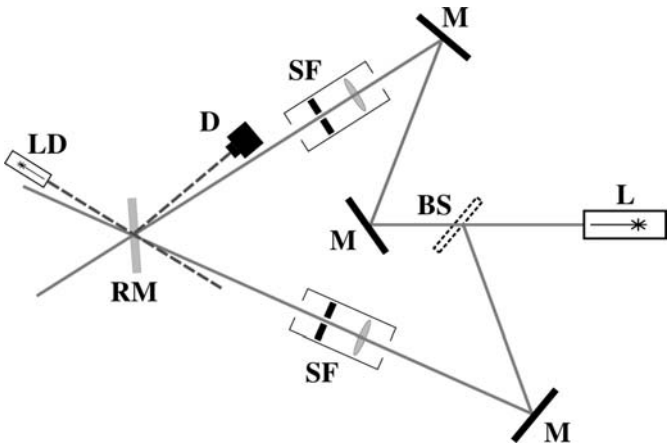

Figure 2. The recording setup for continuous measurement of the diffraction efficiency of the growing grating. L – recording laser, BS – beam splitter, M – mirror, SF – spatial filter, RM – recording material, LD – probing laser diode, D – detector.

The diffraction efficiency η is the ratio of the diffracted intensity and the incident intensity of the probe beam and is associated with refractive index modulation n_1 via the expression derived in the coupled wave theory [11]:

$$\eta = \frac{I_{\text{diff}}}{I_{\text{inc}}} = \sin^2 \frac{\pi n_1 d}{\lambda \cos \Theta} \qquad (\mathbf{1})$$

where d is the thickness of the recording material, λ is wavelength of the probe light, and θ is the Bragg angle. From time evolution of the diffraction efficiency η(t) we can easily obtain a grow-curve of the refractive index modulation $n_1(t)$.

Recording material

Photopolymer recording material, which is prepared and tested in our laboratory, is based on acrylamide monomer and poly(vinyl alcohol) binder [12]. We have optimized the composition of the material to its high performance:

- binder – poly(vinyl alcohol) (35 %)
- monomer – acrylamide (18 %)
- crosslinker - *N*,*N*′-methylenebisacrylamide (2 %)
- plasticizer - acrylic acid (22 %)
- initiator – triethanolamine (23 %)
- sensitizer - erythrosin B (0.05 %)

All components were diluted with water and the solution was spread on glass substrate and dried. The thickness of the tested layer was 90 μm. Due to the sensitizer the recording material absorbs green light with its maximum at 538 nm. The polymerization process (recording) is initiated at 532 nm by illumination. The material does not absorb red light, therefore laser diode at 656 nm can be used for detection without influencing the recording process. The absorption spectrum of the recording material is in Figure 3.

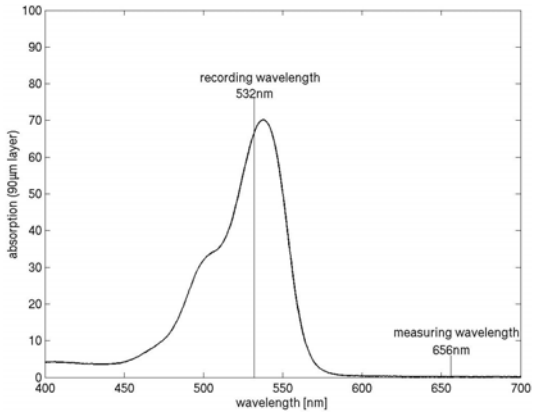

Figure 3. Absorption spectrum of the acrylamide-based recording material with erythrosin B.

Measurement

A typical result of the measurement is given in Figure 4. It is expressed as the time dependence of the refractive index modulation $n_1(t)$. Exposition is started at $t = 0$ and stopped at $t = 1$ s so the exposition time is $t_e = 1$ s. The refractive index modulation and also the diffraction efficiency start to slowly increase and well measurable results are reached after 0.3 s. An increase in the refractive index modulation continues even after the exposition is stopped (laser off) because of the present concentration gradient and still running diffusion process.

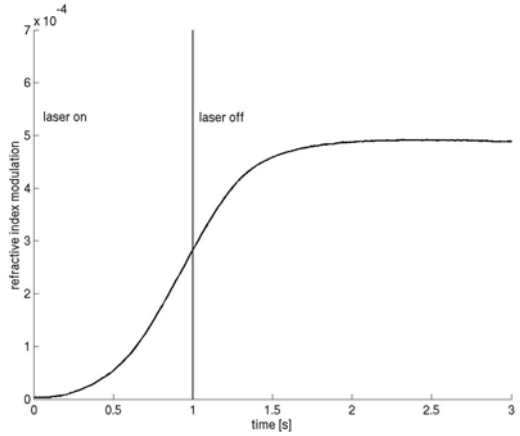

Figure 4. In situ measurement of the refractive index modulation.

Results and discussion

All measurements, which are further presented, were carried out on samples of the recording material described in the previous paragraph. Our samples of the recording materials were tested under varying exposition conditions. Different overall intensities I, different beam intensity ratios and different exposition times t_e were used for diffraction grating recording. Three examples of our results will be given now.

Dependence on exposition time

A series of grow-curves measured on the laboratory material are plotted in Figure 5. The overall intensity I used for each measurement was the same (7 mWcm^{-2}), beam intensity ratio was 1, and spatial period of the recording interference field was 695 nm. As can be seen from the four curves in Figure 5, the highest refractive index modulation is reached for the exposition time 2 s. Clearly, the optimum exposition time is not the maximum one. Especially if the exposition time is kept longer than the optimum value, then degradation occurs and the refractive index modulation decreases. We have tested the material also for other overall intensities I and the optimum exposition time t_e was found different for each recording intensity.

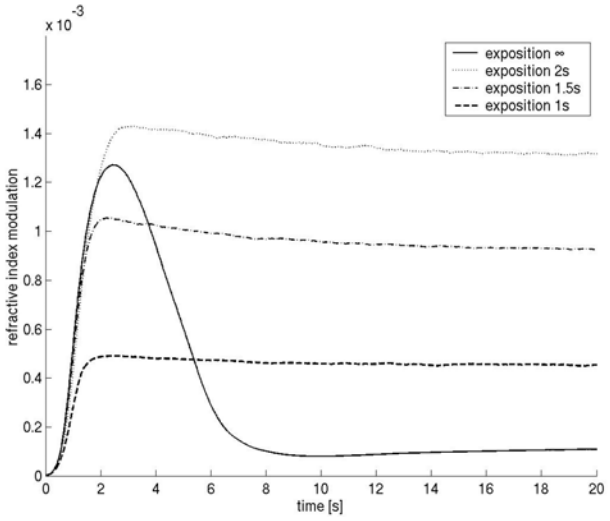

Figure 5. Grow-curves of time evolution of the refractive index modulation for different exposition times.

Testing of the reciprocity law

The exposition energy is the product of the recording intensity and exposition time. For classical recording materials (silver-halide emulsions) an optimum value of exposition energy E_{opt} can be found. When the material is exposed with lower recording intensity, then a longer exposition time is needed to reach the optimum value of exposition energy and vice versa. This is called the reciprocity law (see [13] for details). The relationship $E_{opt} = It_e$ is approximately valid and commonly used in practise. The value of the optimum exposition energy is experimentally determined from diffraction efficiency or refractive index modulation. The exposition energy, which corresponds to the maximum

achievable diffraction efficiency of the recorded grating, is assigned as the optimum one. Based on the previous results, the reciprocity law, which is valid for classical silver-halide emulsions, is clearly not fulfilled for photopolymer recording materials. The optimum exposition energy E_{opt} is not the same for different recording intensities. This can be also seen in Figure 6, where the dependence of refractive index modulation on exposition energy is plotted. Each curve represents a continuous measurement on one sample of the recording material. If the reciprocity law is valid, curves of different recording intensities should have the same course and shape.

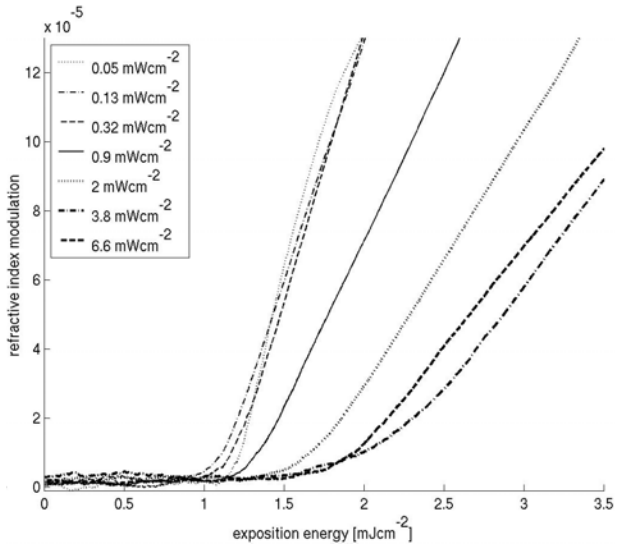

Figure 6. Index modulation versus exposition energy continuously measured during the recording process with different overall intensities.

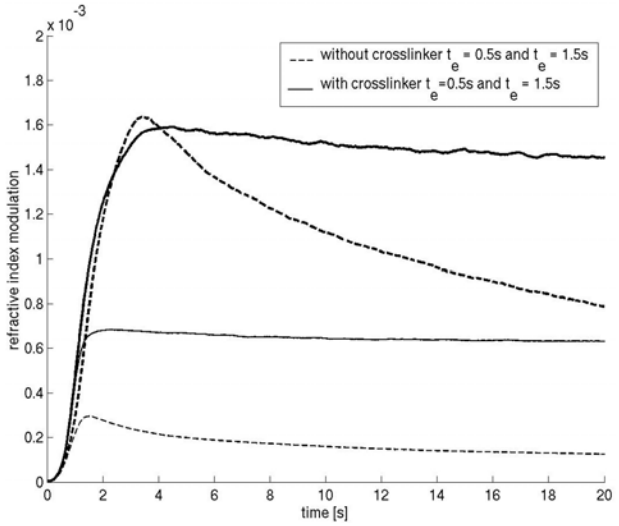

Figure 7. Comparison of materials with (solid lines) and without (dashed lines) the crosslinker.

The influence of crosslinking

For testing the stability of the diffraction grating in photopolymer material, the recording material with and without crosslinker was prepared. It was found that the crosslinker bisacrylamide increases the stability of the diffraction grating, as is documented in Figure 7. Measurements on a material without crosslinker represented by dashed curves and on a material with crosslinker by solid curves. The dashed lines exhibit a large decrease in the refractive index modulation in time and hence degradation of the diffraction efficiency of a grating.
The important role of the crosslinker was confirmed also by other experiments. It seems that the hologram is formed with micronetworks. This assumption is supported by the fact that the exposed material with crosslinker is insoluble in contrast to that without it.

Conclusion

A measuring setup was developed which enabled experimental investigation of processes running during holographic recording in photopolymer recording materials. An acrylamide-based recording material with simple chemical composition was prepared and tested. Based on our experimental studies, the material was optimally designed. Measured grow-curves of refractive index modulation help in clarifying the real behavior of the recording material. It was found that the existing diffusion model cannot explain all effects and hence it is necessary to refine it. Finally, it was proved that branching and crosslinking of polymers improves the stability of the recorded hologram.

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