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The Experimental Study of Acrylamide Based Photopolymer Recording Materials for Applications in Optical Holography

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Summary: The photopolymer recording material based on acrylamide monomer has been experimentally studied. After illumination with an interference field, the photopolymerization process is initiated and a diffraction grating is formed in real-time. The performance of the material depends on its chemical composition and recording parameters. Due to its self-developing characteristics, the real-time measurement of hologram formation is used for detection of the recording process. From the measurement, properties of the material can be determined and optimized for different holographic applications.

Keywords: diffraction grating; holography; photopolymerization; recording material; refractive index

Introduction

Photopolymer recording materials are attractive media for the optical holography, diffractive optical elements, or holographic memories.[1] The recording mechanism is based on the light induced polymerization of molecules of a monomer which has different refractive index from the polymer matrix. Light, in the form of an interference field, with the spatially varying optical intensity is used for illumination. The varying optical intensity reproduces in the variations of polymer density during the exposition process. The local changes of the refractive index are proportional to the changes of polymer density and so a holographic structure is created. Recording materials of this type are known since late 1960's of the last century. They are also commercial available (DuPont, Polygrama), but spectrum of their properties and so possible applications are limited. Each holographic application requires slightly different properties such as the value of the refractive index modulation, spatial resolution, sensitivity, thickness of the layer, or type of the substrate. Some properties can be adjusted when the chemical composition is modified; some of them depend on the recording process. In case of commercial materials, modification of the composition is not possible and therefore we performed our studies on the self-prepared photopolymers. Acrylamide photopolymers are used because they can be prepared easily and they have good characteristics for experimental purposes. The experiments are done on the apparatus enabling the real-time measurement of a hologram growth. The apparatus has been built up in the holographic laboratory of the Department of Physical Electronics.

Recording Material

For the measurements and testing, we have used the acrylamide based recording materials. Most of the measurements were done

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on materials the composition of which is as follows: polyvinyl alcohol 13% w/w (binder), acrylamide 5.5% w/w (monomer), N,N′-methylene-bis-acrylamide 0.6% w/w (crosslinker), acrylic acid 6.5% w/w (co-monomer), triethanolamine 6.7% w/w (electron donor), and erythrosine B 0.01% w/w (optical sensitizer). The components were dissolved in water (68% w/w in mixture) and the prepared water solution was spread on a glass substrate and dried. The thickness of the dried layer was approximately 60 μm. The material is sensitive to green light (maximum sensitivity 538 nm) and it does not absorb light from the red part of the visible spectrum. The commercial available chemicals were used without further purification. The materials with similar chemical compositions were already used for holographic experiments (see[2–4,8]). When the material is illuminated with green light the radical polymerization process, in which polyacrylamide is produced, starts and proceeds.

Experimental Part

Continuous measurement of the diffraction of a beam which passes through the forming grating is the basic principle of the real-time characterization method. It has been already used e.g. in[5–8] and our setup uses the same principle. The detection must not influence the recording process and therefore the wavelength of the detection laser is chosen from the non-absorption band of the material. In contradiction, the recording laser is tuned to the maximum of the absorption band.

The scheme of the setup used in our laboratory is given in Figure 1. The beam of the recording laser is expanded and collimated. One half of it comes through the material directly and the second half is reflected by the mirror. Both then overlap at the recording material and form the interference field which is recorded. For purpose of diffraction efficiency measurement, the material is illuminated with collimated laser diode adjusted at Bragg angle. The recording process can be non-linear; higher harmonics of the refractive index profile can be formed. Therefore we have recently adapted our equipment also to the measurement of the second harmonic frequency of the grating. To obtain the non-harmonic profile another collimated laser diode is used and adjusted at the Bragg angle, which corresponds to the second harmonic grating, and its diffraction efficiency is measured.

The diffraction efficiency is defined as the ratio of the diffracted intensity (measured with detectors) and the incident intensity of the probe beam from the laser diode. The efficiency η_1, respectively η_2, and the first harmonic amplitude n_1, respectively second harmonic amplitude n_2, of the refractive index are connected through Equation (1). The first equation was derived by the coupled wave theory[9] and the second one is the result of the more refined theory.[10]

$$\eta_1 = \sin^2\left(\frac{\pi n_1 d}{\Lambda \cos\Theta_1}\right),$$
$$\eta_2 = \sin^2\left(\frac{\pi d}{\Lambda \cos\Theta_2}\left[n_2 - \frac{n_1^2}{n_0 \sin^2\Theta_2}\right]\right). \tag{1}$$

In Equation (1), d is the thickness of the material, λ is the wavelength of probe light, Θ_1, and Θ_2 are the Bragg angles for the first and second harmonic grating. The results of our measurements are the time dependencies of the refractive index modulations $n_1(t)$ and $n_2(t)$ which we call grow-curves.

Results

Some results of measurements of different research groups have been already published in.[5–8] Commercial available DuPont's photopolymers and acrylamide based photopolymers were tested and grow-curves were obtained. They are qualitatively similar to our results which were presented also in.[11,13] Our measurements are performed on acrylamide based

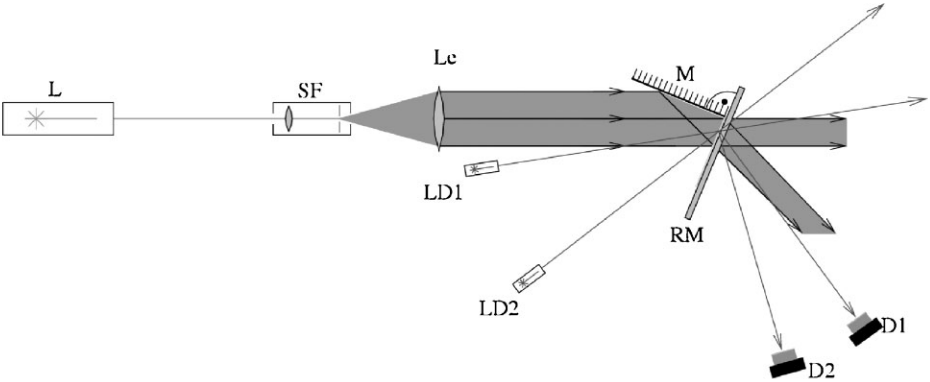

Figure 1.
The recording setup: L – recording laser (Nd:YAG @532 nm), SF – spatial filter, Le – collimating lens, M – mirror, RM – recording material, LD1, LD2 – laser diodes (@656 nm), D1, D2 – detectors.

materials with improved composition and our setup is enhanced of the second harmonic grating detection.

Here we put down some of our measurements which illustrate the dependence of the quality of the creating hologram on the intensity of the recording laser, exposition time, and presence of the crosslinker in the material. Also the graph illustrating limits of spatial resolution of the creating grating is added. These are the results the discussion of which is very important in testing our immobilization-diffusion theory of the grating growth.[14]

The recording intensity influences the polymerization rate and hence the whole recording process. In Figure 2, the grow-curves describing the grating growth recorded by high and low intensity of the laser are given. In the case of the high intensity, the process of formation is faster, but additional effects such as second harmonic grating formation or re-diffusion may occur if the exposition continues too long. In the case of low recording intensity, the refractive index modulation grows up slowly but continuously and the second harmonic grating is weaker.

In Figure 3 grow curves of the refractive index modulation with different exposition times ($t_e = 1,\ 2,\ 4, \infty\,\mathrm{s}$) are presented in Figure 3. The point of the interruption of the exposition is illustrated with the appropriate vertical line. When the illumination of the material is switched off the polymerization process

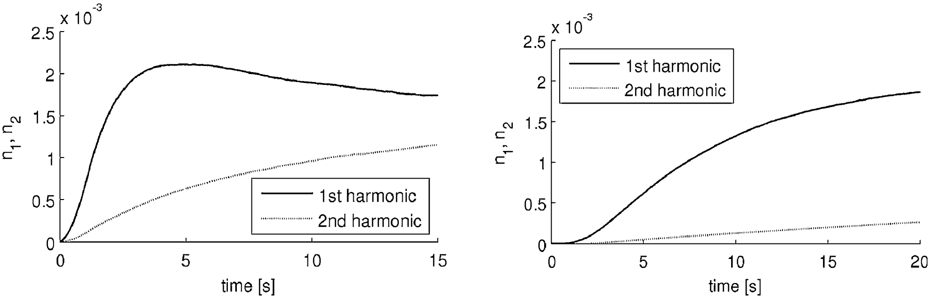

Figure 2.
Grow-curves of the refractive index modulations (first and second harmonics) for high (the left figure, 7 mW/cm^2) and low (the right figure, 0.3 mW/cm^2) recording intensity. The spatial period of the interference field was 1500 nm.

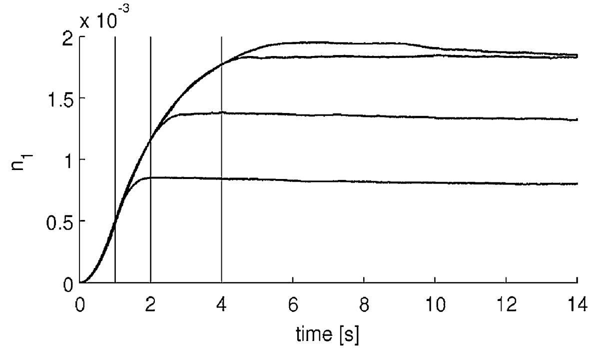

Figure 3.
Grow curves of the refractive index modulation for different exposition times (1, 2, 4, ∞ s). The spatial period of the recording interference field Λ was 700 nm and overall recording intensity was 7 mW/cm^2.

gradually ceases. The probable cause consists in presence of radicals which were generated during the exposition process and which remain for some more time after the exposition in the material. The polymerization process continues till they recombine and hence the refractive index modulation still grows. We have noticed that relative increase of the second harmonic modulation after interrupted exposition is much smaller than the first harmonic modulation. Therefore the interrupted exposition prevents unwanted effects which reduce efficiency and increase noise of the grating. Also the interference field is not stable enough for long exposition. The optimal exposition time for the sample in Figure 3 is about 4 s.

The maximum achievable refractive index modulation n_1 depends on the spatial period Λ of the recording interference field. The material response on the spatial period is called the spatial resolution of the recording material and is presented in Figure 4. As can bee seen, the resolution of the acrylamide based material is limited; recording of very short spatial periods is not possible. It is probably caused by the length of polymer chains which are formed during the exposition process. Because of this limit the material is not suitable for recording of reflection holograms which require very high spatial resolution.

We have done several tests for optimization of the chemical composition of our laboratory prepared recording material. As

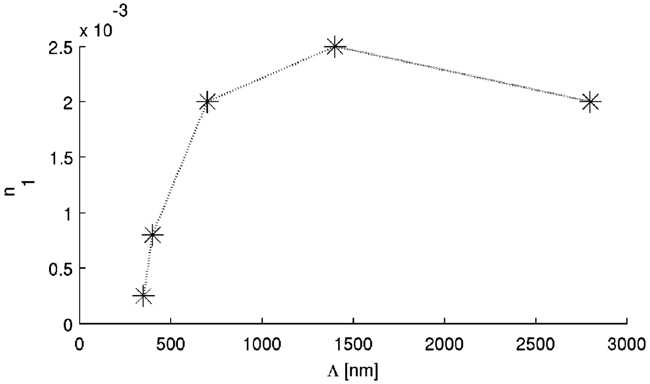

Figure 4.
The resolution capacity for the acrylamide based recording material. The overall intensity for all measurements was 7 mW/cm^2.

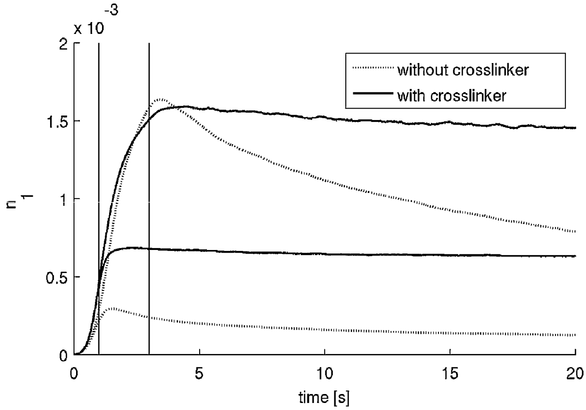

Figure 5.
Influence of the crosslinker on the long-termed stability of the formed grating. Exposition times 1 and 3 s, the spatial period 700 nm, and the overall intensity 7 mW/cm^2.

an example, the measurements of grow-curves, which justifies the presence of crosslinker, is illustrated in Figure 5. When the crosslinker is added to the material the refractive index modulation does not drop so much after the exposition and the grating is much more stable. The crosslinker causes formation of micro-networks which hinder the possible re-diffusion process of formed polymer chains and the decrease of the refractive index modulation.

Conclusions

An experimental study of acrylamide based recording materials has been done. We have built up and used the experimental equipment to obtain grow-curves of recording materials with different composition and at different exposition conditions. It is a large advantage of the method that for photopolymers the real-time characteristics (grow-curves) of the hologram growth may be obtained. The results help us to optimize the material response for different holographic applications. Next to the measurement, the theoretical model of the recording process has been developed.[12,14] With the model, it is possible to simulate and predict the behavior of the prepared material and so to reduce the number of experiments necessary to its optimization.

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