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Optimisation of an Acrylamide-based Photopolymer System for Holographic Inscription of Surface Patterns with Sub-micron Resolution

Kevin Trainer
Drexel University

Kevin Wearen
Technological University of Dublin

Dimana Nazarova
Bulgarian Academy of Sciences

See next page for additional authors

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Authors

Kevin Trainer, Kevin Wearen, Dimana Nazarova, Izabela Naydenova, and Vincent Toal

Optimisation of an acrylamide-based photopolymer system for holographic inscription of surface patterns with sub-micron resolution

K Trainer[1], K Wearen[2], D Nazarova[3], I Naydenova[2],[3]*, V Toal[2]

[1]Department of Physics, Drexel University, Philadelphia, USA; UREKA student, FOCAS Institute, Dublin 8, Ireland
[2]Centre for Industrial and Engineering Optics/School of Physics, Dublin Institute of Technology, Dublin 8, Ireland
[3] Central Laboratory of Optical Storage and Processing of Information, Bulgarian Academy of Sciences, Bl. 101, Acad. G. Bonchev Str., 1113 Sofia, Bulgaria
Corresponding author e-mail: izabela.naydenova@dit.ie

Abstract We describe the optimisation of the holographic patterning of sub-micrometer surface relief structures in an acrylamide-based photopolymer. A substantial improvement in the photoinduced surface relief resolution was achieved by altering the photopolymer chemical composition and by introducing a single step post recording thermal treatment of the layers. It was observed that, by optimisation of the chemical composition of the photopolymer layers, the maximum achievable spatial frequency increases from 200 l/mm to 550 l/mm. The improvement of the surface relief amplitude by alteration of the chemical composition is limited due to the fact that both decrease of the plasticiser and increase of the monomer concentrations result in less stable photopolymer layers. In order to obtain further improvement in the spatial frequency resolution a thermal treatment of the layers was implemented. It was observed that baking of the layers at temperatures ranging from 120 to 220°C at a rate of 1°C /min makes possible the inscription of surface relief profiles with a sub micrometer period of 650 nm and amplitude of 15 nm.

Keywords: holographic patterning, surface relief structures, holographic gratings, photopolymers, self-processing photopolymers
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1. Introduction

The development of new photopolymers for holographic recording has importance for a number of different applications: holographic sensors, electro-optical switchable holographic devices, holographic data storage and the design and fabrication of holographic optical elements. A self-developing acrylamide-based photopolymer has been successfully developed at the Centre for Industrial and Engineering Optics for more than a decade. It has been observed that with particular geometries of holographic recording in these materials in addition to the volume holograms, surface relief modulation is inscribed [1-3]. Optically recorded surface relief modulation has been previously observed and characterised in other photopolymer systems [4-7]. A common feature of the process of optically inscribed surface relief modulation in self-processing photopolymerisable materials is its limited spatial frequency resolution. It is observed that the amplitude of the surface relief profile decreases with the increase of the spatial frequency and the upper resolution limit in these materials does not exceed 500 l/mm. The lack of high spatial frequency response in self-processing photopolymers is currently ascribed to surface tension that prevents the surface deformation at high spatial frequencies. For many practical applications such as fabrication of switchable electro-optical devices [8-10] and design of optical sensors [11-12] sub-micron resolution is required. Such high spatial resolution is achievable by photolithography or electron beam lithography, but both techniques are expensive and the first requires wet chemical post processing of the material while the second one is characterised by a small throughput. Optical patterning of photosensitive materials' surface with sub-micron resolution has been achieved in azopolymers [13-16], but they are relatively expensive materials and cannot be bought off the shelf. The acrylamide photopolymer described in this paper is prepared from off the shelf chemicals, it has low cost, can be easily deposited on large areas and on a variety of substrates, including plastic, it is characterised by high sensitivity ($1.4.10^3$ cm/J at 532nm) and long shelf life, which makes it a material suitable for industrial applications. Here we report our recent results from the improvement of the surface relief modulation spatial frequency response of an acrylamide-photopolymer. Based on our understanding of the mechanism of surface relief formation in this material [1-3] a systematic alteration of its chemical composition was carried out. Additionally, a one step, dry post-recording treatment of the recorded surface relief structures was introduced. A remarkable improvement from previously measured 5 nm at 200 l/mm [1] to 15 nm at 1550 l/mm has been achieved. We believe that this study provides a useful basis for further improvement of the surface relief spatial frequency resolution in acrylamide-based photopolymers.

2. Background

2.1 Surface Relief Grating (SRG) formation in acrylamide-based photopolymers

When a holographic transmission diffraction grating is recorded in an acrylamide – based photopolymer, a surface relief grating can be formed in addition to the volume holographic grating. The recording medium under study consists of a binder in which two monomers, an electron donor, and a photosensitive dye are dissolved. The simultaneous formation of volume and surface relief gratings, is due to a polymerisation driven diffusion of photopolymer components. The polymerization consists of three distinct steps: initiation, propagation and termination. The initiating step is the generation of a free radical. The free radical is produced when the photosensitive dye, absorbs a photon of light in the presence of an electron donor. This free radical attacks the carbon-carbon double bond of the acrylamide monomer, attaching itself, thus making the monomer a free radical. The free radical monomer now reacts with another monomer, and the polymerization chain begins to propagate. The chain terminates when two free radicals combine and the chain stops growing.

To record a holographic diffraction grating, laser light is split into two beams that are then redirected to overlap and interfere on the surface and throughout the volume of the photopolymer layer. Because the monomer only begins to polymerize in bright regions of the interference pattern, a concentration gradient is created and a diffusion process begins. Unpolymerized acrylamide in the dark regions begin to diffuse into the bright regions, where it is subsequently polymerized. Previous studies of the process of SRG formation reveal that the monomer mass transport is mainly responsible for the formation of surface relief peaks. This was supported by observation of the locations of the surface relief peaks with respect to the interference pattern [1] and by the dependence of the surface relief amplitude on the intensity of recording.

2.2 SRG applications

The importance of SRGs has already been shown in the formation of an electro-optical switchable device [10]. In this application, SRGs are filled with liquid crystals that are characterised by an ordinary refractive index identical to that of the adjacent photopolymer layer. These liquid crystals could be aligned using an applied voltage. Once aligned, light no longer was diffracted when passing through the layer because of the disappearance of the refractive index modulation. The devices were fabricated using SRGs of 100 l/mm spatial frequency. For practical applications where more compact systems are sought and better alignment of the liquid crystal molecules is required, higher spatial frequencies would be beneficial.

Another potential application utilizing SRGs is holographic sensors. Two main objectives must be realized: surface periodicity and high spatial frequency (>1300 lines/mm) formation of SRGs. Periodicity is important so as to take advantage of Surface Plasmon Resonance (SPR) and high spatial frequencies are necessary so that the transmission spectrum appears in the visible region. Nazarova et al. have already demonstrated that the shift in the spectral position of the resonance peak can be used to determine very low concentrations of nanoparticles suspended in the host matrix [11].

3. Experiment

3.1 Materials

The photopolymer layer consists of a polyvinyl alcohol binder, two monomers- acrylamide and N,N'-methylenebisacrylamide [17], triethanolamine as an initiator and erythrosin B photosensitive dye. Once mixed, 0.3 ml of the solution was spread on a 75 mm x 25 mm glass substrate. The films were ready for use after drying for ~5 hours. Layer thickness typically averaged about 30 μm.

3.2 Experimental set-up

The photoinduced surface relief was inscribed by recording transmission holographic gratings of spatial frequency ranging from 200 – 1550 lines/mm. A Verdi™ laser (532 nm) was used for holographic recording. The optical set-up is shown in figure 1. The spatial frequency of recording was adjusted by moving the sample along a rail as well as adjusting the mirror (see Fig. 1). The recording intensity was varied between 10 and 30 mW/cm². Exposure time was varied between 10 and 100 seconds.

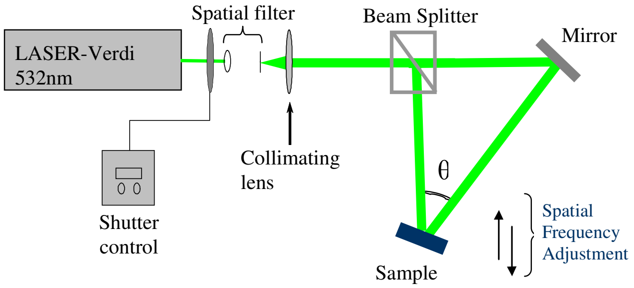


Fig. 1. Optical set-up for recording SRG.

For correlation of the position of the peaks and the bright and dark areas, the sample was illuminated through a spatial light modulator (SLM). Two types of patterns were written on the modulator and then imaged onto the photopolymer layer.

The photopolymer surface was studied using a white light interferometric (WLI) surface profiler MicroXAM S/N 8038 and an atomic force microscope AFM EasyScan model 2. These two methods both reveal the surface profile of the structure, with each providing attractive qualities. The WLI delivers fast and reliable information with resolution of 1000 l/mm, whereas the AFM delivers a much higher resolution picture, albeit requiring more time.

4. Results and Discussion

As the main goal of this experimental work was to form SRGs with sub-micrometer periodicity, the influence of the different sample compositions, recording parameters and post-recording treatments on the surface relief amplitude were studied. For each experimental data point three different samples were studied and measurements were carried out at least two different locations on the surface of each sample.

4.1 Triethanolamine (TEA) variation studies

TEA role in the photopolymer composition is a dual one - as an electron donor participating in the free radical generation and as a plasticizer determining the maximum amount of monomer that can be accommodated by the PVA matrix without phase separation. Previous studies revealed [3] that increasing the plasticizer concentration results in decrease in the surface relief amplitude. In order to achieve the opposite effect the TEA amount in the photopolymer mixture was decreased in steps from 2 ml to 0.5 ml which resulted in decrease of the plasticizer concentration in the dry photopolymer layer from 47 % w/w to 27 %w/w. The remainder of the photopolymer mixture in this particular experiment consisted of 0.6 g acrylamide, 0.2 g of N,N'-methylenebisacrylamide, 17.5 ml of 10 % w/v PVA stock solution and 4 ml of 1.1 M dye stock solution.

As shown in Fig. 2, as the TEA concentration is reduced, the SRG amplitude increases. Notice that the highest SRG amplitudes were obtained at 27 % w/w TEA concentration; however, layer stability became an issue in the form of local crystallization of acrylamide monomer. Therefore, obtaining higher surface relief amplitude by this method was sacrificed in exchange for more stable layers and thus the sample with

31 % w/w TEA concentration was chosen for further optimisation.

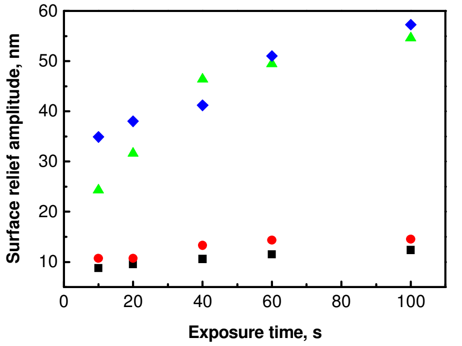


Fig. 2. Surface relief formation as a function of TEA concentration – 47 % w/w (2 ml) (■), 40 % w/w (1.5 ml) (●), 31 % w/w (1ml) (▲) and 27 % w/w (0.5 ml) (♦). Recording performed at 200 lines/mm, recording intensity was 10mW/cm^2.

In parallel with the TEA concentration studies, optimum exposure conditions were also determined. Previous studies [1-3] revealed that a recording intensity of 10 mW/cm^2 is favourable for obtaining high SRG amplitude. Thus the intensity was held constant at this level and exposure time was varied- from 10 s to 100 s. As it is seen from Fig.2, except for the sample with the lowest TEA concentration, there is a saturation of the surface relief amplitude when the exposure time approaches 100 s. As the layer composition with 31 %w/w TEA concentration was chosen for further optimisation the exposure time was used in subsequent experiments was 100 s.

4.2 Spatial Frequency Limitation

Once the optimum TEA concentration for obtaining maximum SRG amplitude at 200 l/mm was determined, the new limiting spatial frequency was sought. Using the previously determined exposure parameters (intensity of 10 mW/cm^2 and exposure time 100 s), holographic diffraction gratings were recorded at various spatial frequencies; beginning at 200 lines/mm and progressing higher until SRGs were no longer formed. From these studies, a new limiting spatial frequency of 500 lines/mm was found (Fig.3). At this spatial frequency the surface relief amplitude was 1nm. The inability to achieve SRGs at higher spatial frequencies is commonly explained by the surface tension that prevents the surface from deforming when the spatial frequency increases and the surface relief peaks come closer together.

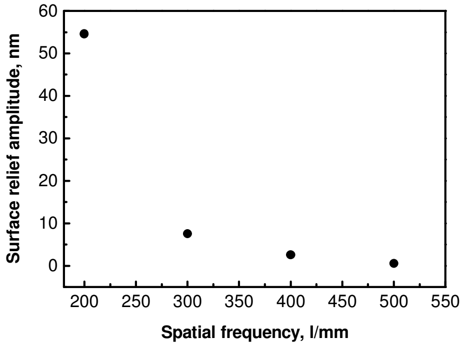


Fig.3 Spatial frequency response of surface relief modulation in layers containing 31 % w/w TEA. The recording intensity was 10 mW/cm^2 and the recording time was 100 s.

4.3 Effect of post-exposure illumination

The influence of different types of post-exposure irradiation was studied. The layers were recorded by illumination with an interference pattern with spatial frequency of 300 l/mm. The recording exposure was kept constant - 1J/cm^2 and the intensity and exposure times were varied accordingly. Three different intensities were studied – 10, 20 and 30 mW/cm^2. After recording the layers were exposed to light and then the surface relief amplitude was measured. The purpose was to further polymerize any residual monomer. Two different light sources were used – an UV light source (Mega Electronics Limited LV202, 2.5 mW/cm^2) and an ordinary room light. In both cases an increase in the SRG amplitude was observed. A possible explanation for this enchancement of the SRG amplitude is the following: photopolymerization causes a reduction in volume in the bright regions of the interference pattern, but shortly after that mass transport of monomer from dark to bright regions driven by the monomer concentration gradient causes the volume in the bright regions to increase and ultimately exceed its initial value. At the end of the holographic recording there is more unpolymerised monomer in the dark than in the bright areas. The post-exposure spatially uniform illumination polymerizes the residual monomer in the dark regions of the interference pattern and decreases their volume thus producing an increased SRG.

Comparing the results for the two light sources it was determined that the SRG amplitude was always higher when UV post exposure was used (Fig.4).

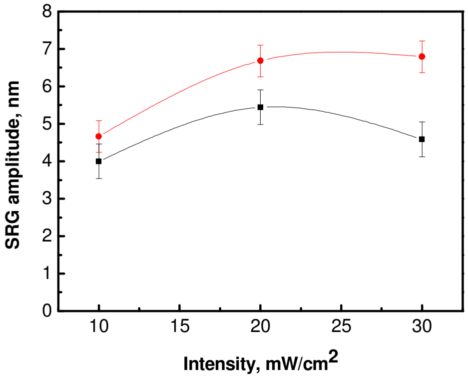


Fig. 4 Influence of the post-recording UV light (●) and ambient room light (■). Samples were recorded at 400l/mm, total exposure 1J/cm^2.

4.4 Effect of variation in monomer concentration

The post recording treatment by light revealed that it might be possible to increase the surface relief amplitude if more non polymerised monomer molecules were left in the dark regions and later cause to polymerise either by illumination with light or by some other means. That is why the second polymer component concentration to be studied was that of the acrylamide monomer. This experiment sought to study the relationship between monomer concentrations and SRGs amplitude. The SRGs form initially because of a mass transport of monomer when exposed to interfering beams of laser light. Therefore, the monomer plays a crucial role in the overall SRG formation process as well as in the post recording SRG enhancement process. Samples were prepared with a monomer concentration 50 percent greater than in the original photopolymer recipe - 0.6 g Acrylamide, 0.2 g of N,N'-methylenebisacrylamide, 1 ml of TEA, 17.5 ml of 10 % w/v PVA stock solution and 4 ml of 1.1 M dye stock solution. The monomer concentrations were in the range from 8.8 %w/w to 22.5 % w/w of the dry layer. After obtaining the dry layers, the samples were illuminated with a holographic pattern of spatial frequency of 400 l/mm and then their surface relief amplitude was measured directly, without exposure to any UV or ambient room light. After that the layers were baked repeatedly for 10 min at a time at 120 °C and the SRG amplitude was measured after each baking step. It has been previously reported [18] that acrylamide polymerisation occurs on exposure to elevated temperatures and it was expected that the baking of the samples would polymerise the remaining monomers in the dark regions. The results of this experiment are presented in

Fig.5. As it is seen from the figure there is a direct relationship between monomer concentration and SRG amplitude increase after post recording thermal treatment. What is also evident is that immediately after the recording, before any post-recording treatment, the SRG amplitudes were measured to be almost identical. This could be due to the fact that, regardless of the initial monomer concentration, a similar (or identical) percentage of monomer becomes polymerized at constant recording conditions, meaning that a similar (or identical) mass was transported between the dark and bright regions. The higher increase of the SRG amplitude for samples containing higher monomer concentration supports the hypothesis that the SRG increase is due to shrinkage in the dark regions due to polymerisation of the residual monomer. The increase reached saturation much earlier (after the second baking) for the sample containing the lowest amount of monomer (the red dots in Fig.5). For the samples with 20.5 %w/w monomer concentration the SRG amplitude didn't reach saturation within the 4 cycles of baking. For the two higher concentrations any more than 3 cycles of baking led to a decrease in the SRG amplitude.

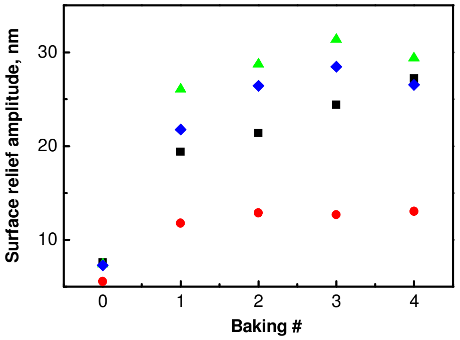


Fig.5 Dependence of the surface relief modulation on the acrylamide monomer concentration after repeated baking for 10 min at 120 ºC– 8.8 % w/w (●) , 11.5 % w/w (■) , 20.5 % w/w (♦) and 22.5 % w/w(▲). Spatial frequency of recording was 400 l/mm, recording intensity was 10 mW/cm^2 and recording time was 100 s.

4.5 Effect of elevated temperature post-recording

In order to study the effect of the second type of post-exposure treatment in detail the recorded samples were exposed to elevated temperatures from 120 ºC to 220 ºC. Samples with the following chemical composition were studied in this experiment 0.9 g acrylamide (22.5 %w/w), 0.2 g N,N'-methylenebisacrylamide, 1 ml TEA (28.5 % w/w), 17.5 ml of 10 % w/v PVA stock solution and 4ml of 1.1M Erythrosine B stock solution. The upper temperature limit was imposed by the operational limit of the oven used in this experiment. After recording at spatial frequency of 400 l/mm the samples were measured using the WLI and then were placed in the oven at the set temperature. The samples were baked at this temperature for 10 min then were taken out and their SRG amplitude and mass were measured. Meanwhile the oven temperature was changed and allowed to reach equilibrium. The samples were put back in the oven and the same procedure was repeated for all temperatures in the range from 120 to 220 ºC. The results from this experiment are presented in Fig. 6.

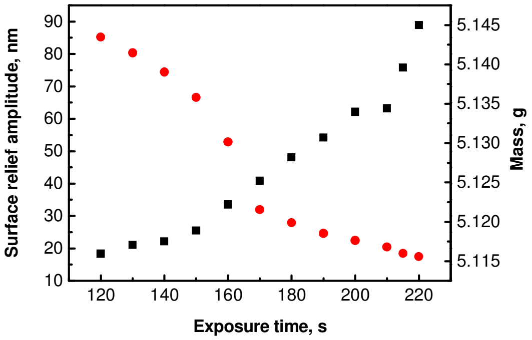


Fig.6 Study of the influence of thermal post-exposure treatment on the SRG amplitude (■) and on the mass (●). The chemical composition of the samples was as described in section 4.5. Spatial frequency of recording was 400 l/mm, recording intensity was 10 mW/cm^2 and recording time was 100 s.

As is seen in figure 6 a consistent increase in SRG amplitudes at temperatures above 120 ºC was observed. As is evident from the figure, two slopes define the SRG amplitude curve. The first applies between values of 120 and 150 ºC. The second, and steeper slope, applies from 150 ºC and above. A parallel measurement of the sample mass revealed that there is a reduction in mass as the baking was carried out (data included in Fig.6).

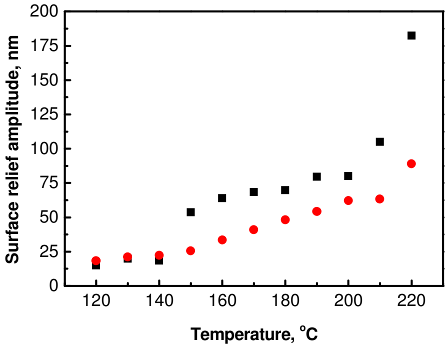


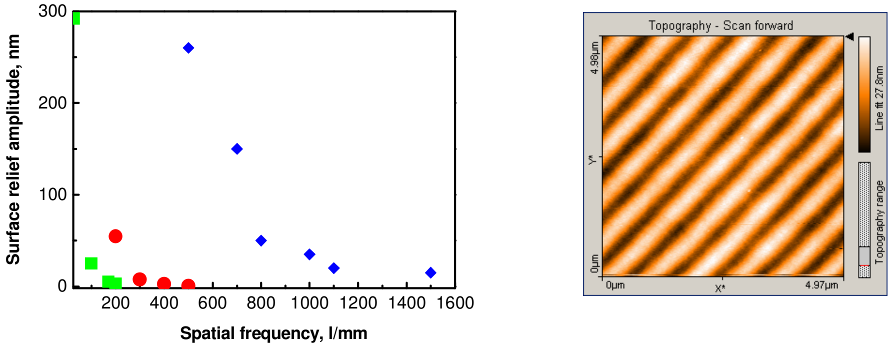
Fig.7 Comparison of the two modes of thermal treatment – continuous (■) and interrupted mode of baking(●).The chemical composition of the samples was as described in section 4.5. Spatial frequency of recording was 400 l/mm, recording intensity was 10 mW/cm^2 and recording time was100 s.

To optimise the baking procedure, a continuous baking experiment was also carried out. For this, 22 samples were placed in the oven set to 120 ºC. Every ten minutes, two samples were removed and the oven temperature was increased by 10 ºC until the oven reached 220 ºC. Two samples were in the oven for a total of 120 minutes. As seen in Fig.7, SRGs increase more by baking continuously than they do in ten minute intervals. The graphs also show similar changes in the slope at around 150ºC for both baking procedures.

4.6 Spatial Frequency Limitation II

In order to determine the new spatial frequency resolution limit for SRG formation, photopolymer layers were recorded using the optimum exposure parameters at spatial frequencies in the range from 500 lines/mm to 1600 l/mm. Each sample was prepared using the optimised chemical compositions as explained in the previous sections. Once recorded, they were baked continuously at temperatures increasing from 120 ºC – 220 ºC by 10 ºC /10 min. The results from this experiment are presented in

Fig.8a. As it is seen from the figure a huge improvement on limiting spatial frequency of the SRG formation from that found from the early studies (500 l/mm) was achieved. Periodical structures were inscribed at a spatial frequency of 1550 l/mm. The surface relief profile was studied by AFM and it was determined that the amplitude of the recorded SRG was 15 nm (see Fig. 8 b).



a) b)

Fig.8 a) Spatial frequency dependence of the SRG amplitudes: (■) after optimisation of the recording conditions; (●) after optimisation of the photopolymer composition; (♦) after exposure to elevated temperature. b) AFM scan of the SRG of spatial frequency of 1550 l/mm. The amplitude of the SRG was 15 nm.

4.7 Study of the position of the surface relief amplitude peak with respect to the light pattern

A previous study of the position of the SRG peaks with respect to the light pattern was carried out using Dektak profiler equipped with a video camera. The spatial frequency of the grating used in this study was 5 l/mm. Here we used a SLM to image two different patterns (Fig. 9a and c) onto photopolymer layers optimised for SRG recording. The resulting surface relief profiles are presented in Fig. 9b and d respectively. The spatial frequency of the pattern was 16 l/mm. From the results in Fig. 9 it is clearly seen that peaks and troughs correspond respectively to the bright and dark rectangles in the pattern confirming once again that mass transport from dark to bright regions is the main mechanism of photoinduced surface relief formation. The samples shown in Fig.9 were not exposed to high temperature. Nevertheless, the amplitude of the surface relief profiles is significant - in order of 4µm. Studies of the influence of the baking on low spatial frequency patterns are currently in progress.

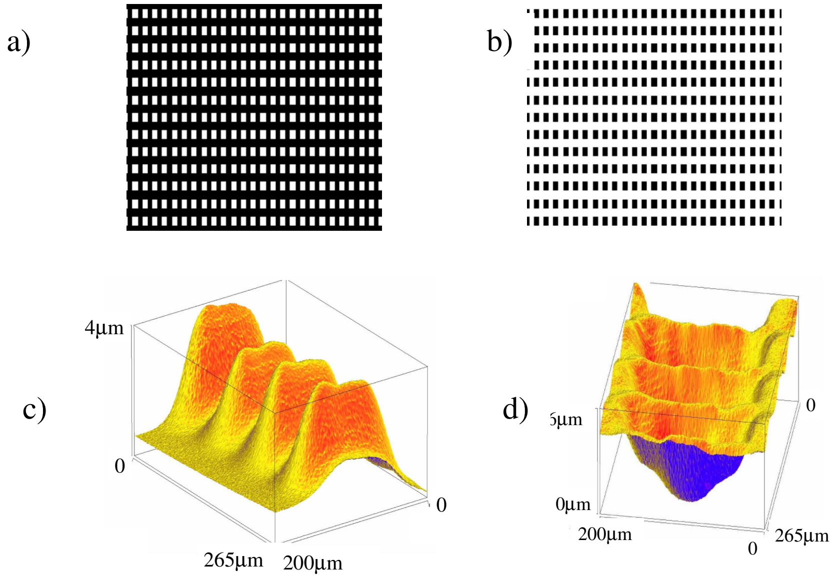


Fig. 9 SLM patterns imaged onto the photopolymer layer a) and c); WLI images of the corresponding photoinduced surface relief profiles b) and d). The spatial frequency of the patterns is 16 l/mm.

5. Conclusions

We have successfully fabricated SRGs at 1550 lines/mm by systematically determining which parameters lead to the formation of the highest surface relief peaks. This includes variation of parameters before, during and after recording. Layer composition was varied and optimized. It was observed that a decrease of the TEA concentration and the increase of monomer concentration both led to higher SRG amplitudes. Exposure parameters such as intensity and time of exposure were also studied and optimised. Finally, post-recording treatment including UV light exposure and baking was utilized to further enhance the surface relief amplitude. From these studies, the optimum surface relief formation procedure was developed and sub-micron resolution surface relief structures were inscribed.

Using illumination through a SLM it was demonstrated that the surface relief profile peaks coincide with the illuminated areas and their amplitude is in order of 4 µm before baking. This could possibly be further improved by baking at elevated temperatures.

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