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Holographic Recording of Patterns in Thin Film Acrylamide-based Photopolymer

Izabela Naydenova

Technological University Dublin, izabela.naydenova@tudublin.ie

Kotakonda Pavani

Technological University Dublin

Emilia Mihaylova

Technological University Dublin, emilia.mihaylova@tudublin.ie

See next page for additional authors

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Authors

Izabela Naydenova, Kotakonda Pavani, Emilia Mihaylova, Katia Loudmer, Suzanne Martin, and Vincent Toal



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Izabela Naydenova

Dublin Institute of Technology, izabela.naydenova@dit.ie

Kotakonda Pavani

Dublin Institute of Technology

Emilia Mihaylova

Dublin Institute of Technology, emilia.mihaylova@dit.ie

Katia Loudmer

University of Bordeaux

Suzanne Martin

Dublin Institute of Technology, suzanne.martin@dit.ie

See next page for additional authors

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Authors

Izabela Naydenova, Kotakonda Pavani, Emilia Mihaylova, Katia Loudmer, Suzanne Martin, and Vincent Toal

Holographic recording of patterns in thin film acrylamide-based photopolymer

I. Naydenova¹, K. Pavani¹, E. Mihaylova¹, K. Loudmer², S. Martin¹, V. Toal¹

¹Centre for Industrial and Engineering Optics, Dublin Institute of Technology,
Kevin Street, Dublin 8, Ireland

²University of Bordeaux 1, 351 cours de la Libération, Bordeaux, France

izabela.naydenova@dit.ie

Abstract

A study of the light induced surface relief modulation in thin photopolymer layers is reported. Due to the nature of the photopolymer used no additional post-processing is required after holographic recording.

An investigation of the dependence of the amplitude of the photoinduced relief modulation on different parameters of recording such as spatial frequency, intensity of the beams and times of exposure has been carried out. The surface relief modulation is characterized by white light interferometry. Photopolymer layer thickness ranges from 1-5 μ m. A model of the mechanism of surface relief formation is proposed on the basis of the measured dependencies.

A variety of patterns are inscribed in order to demonstrate the potential of this photopolymer in the design of different diffractive optical elements.

Keywords: photopolymers, holography, surface relief, thin films, photoinduced patterns, acrylamide

1. Introduction

Single step light induced surface relief is an attractive approach for the design of diffractive optical elements^{1,2} and for assisting the orientation of liquid crystal molecules in some optical devices^{3,4}. In order to optimise the performance of photopolymer based devices it is important to understand the mechanism of surface relief formation in these materials. This will allow controlling parameters such as surface relief amplitude and shape which are expected to be crucial for the final device performance.

In the current paper we report an investigation on the photoinduced surface relief modulation in acrylamide-based photopolymer thin films. A maximum surface relief modulation in the order of 120 nm at spatial frequency of 10 l/mm was achieved using recording times in order of 20 s. The dependence of the photoinduced relief modulation on the spatial frequency, recording intensity and sample thickness were investigated.

2. Theory

2.1. Optical recording in photopolymers

Photopolymers are photosensitive materials that undergo change of the refractive index under illumination with light of an appropriate wavelength. Usually the photopolymer system consists of a monomer, an initiator, sensitising dye and a binder. Initially the binder was believed to be simply a holding matrix for the other components. Since the development of the diffusion based models⁵⁻⁷ describing holographic recording in photopolymers it became clear that the binder plays

a very important role in the ultimate performance of the photopolymer. The binder permeability controls, to a large extent, the diffusion processes during and after holographic recording.

Previous studies of diffusion processes in acrylamide-based photopolymer⁸ reveal that the diffusion of monomer at the beginning of the recording is characterised by diffusion constant that is relatively fast when compared with other photopolymer systems^{9,10}. Such observation would imply that relatively large surface relief amplitudes under light illumination could be expected in this photopolymer system if the diffusion is the main mechanism of surface relief formation.

2.2. Theoretical models for surface relief formation

There are two main models describing the surface relief formation in photopolymers. The first model explains the relief formation by shrinkage of the photopolymer depending on the intensity of light. This model is applicable to the systems where the peaks of the surface relief appear in the non-illuminated areas¹¹. The second model is based on the assumption that redistribution of system components by diffusion is responsible for the relief formation. This fits well with experimental observation of the surface relief peaks appearing in the illuminated areas. There have been suggested different reasons leading to diffusion of the components – a monomer chemical potential¹ gradient, concentration gradient of monomer² and local shrinkage of a polymer layer¹². All of the proposed models consider the change in the surface free energy during the relief formation as the main reason for the restricted resolution of the inscribed relief structures^{1,2,11,12}.

In the analysis of the surface relief formation in thin photopolymer layers, a new factor must be considered in addition to the above mentioned factors. When the thickness of the layers approaches few micrometers the interaction between the photopolymer and the substrate appears to play an important role in the ultimate surface relief amplitude and shape.

3. Experimental

3.1. Materials

The photopolymer solution was prepared as described elsewhere⁸. It consisted of a polyvinyl alcohol binder, two monomers – acrylamide and N,N'-methylenebisacrylamide, Erythrosin B sensitising dye and triethanolamine as an initiator. The photopolymer system is water-soluble. The components were mixed with the help of a magnetic stirrer for 60min. The dye was added at the final stage. Two different approaches were used to obtain thin layers – spin coating and gravity settling. Spin coating was performed on 150 μ m thin square shaped substrates with dimensions of 2.5x2.5 cm². In order to obtain layers with thickness of 2 μ m the rate of rotation was 2800 RPS. The layers were dried for 3 hours before they were used for holographic recording. For use in gravity settling preparation the photopolymer solution was 20 times diluted with deionised water. Then it was spread on glass plates with dimensions of 5x5 cm². Depending on the amount of the solution spread on the substrate, from 0.5 to 2ml, films with good optical quality and thicknesses from 1 to 5 μ m were obtained. The samples were ready for use after drying for 24 hours at constant humidity of 60%.

3.2. Experimental set-up

The photoinduced surface relief was inscribed by holographic recording of transmission diffraction gratings with spatial frequency in the range of 8 - 250 l/mm. The second harmonic of a Verdi 05 NdYtVO₄ laser at 532 nm was used to record the gratings. Two different holographic set-ups were used for recording gratings with spatial frequencies above 100 l/mm (Fig. 1a) and below 100 l/mm (Fig. 1b). The first set-up was a standard holographic optical set-up. The spatial frequency of recording was altered by changing the position of one of the mirrors and so changing the angle between the two recording beams. The recorded gratings were unslanted. This was ensured by positioning the sample to ensure that the sample normal coincided with the recording beams bisector. The second set-up was a Michelson type interferometer and the change in the spatial frequency was achieved by rotation of one of the mirrors.

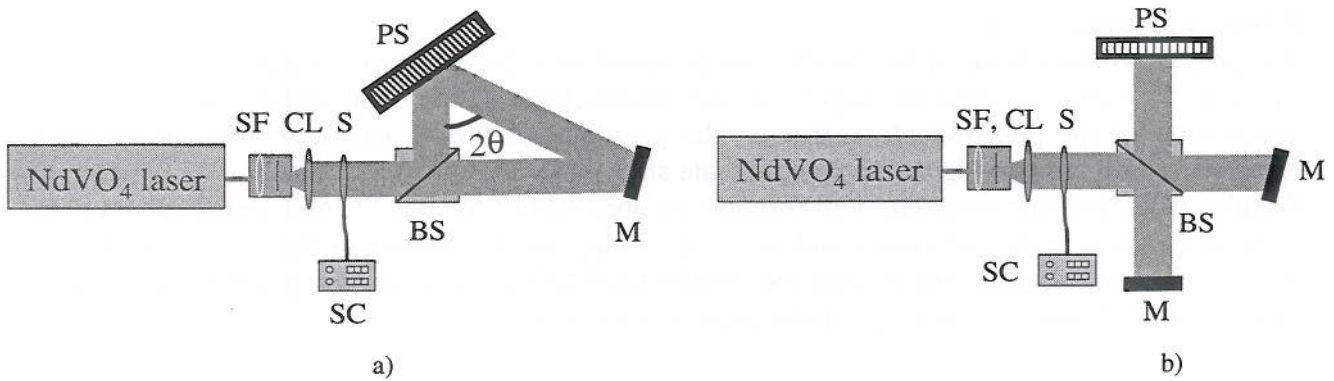


Fig.1 Holographic set-up for recording at spatial frequencies above 100 l/mm a) and below 100 l/mm b), SF- spatial filter, CL- collimating lens, PS – photopolymer sample, M- mirror, S – shutter, SC – shutter controller.

For recording more complicated 2D patterns the sample orientation was changed between two consecutive recordings (crossed grating) as shown on Fig.2.

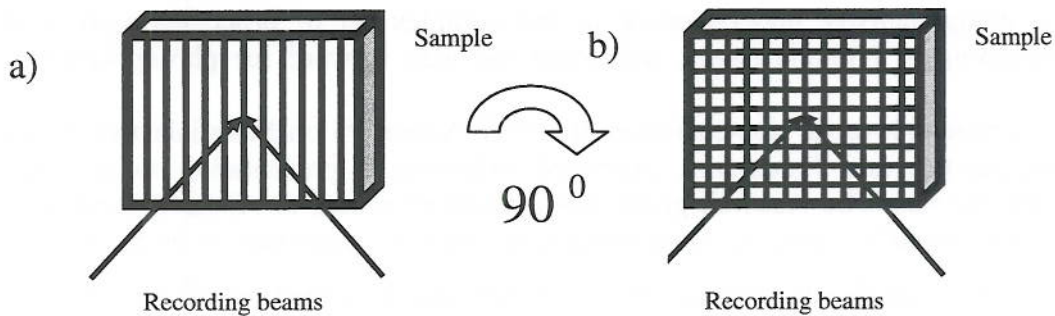


Fig. 2 Recording of patterns. After recording of the first grating a) the sample is rotated at 90° and a second grating with the same spatial frequency is recorded.

The recording intensity was varied in the range 1-25 mW/cm². In order to observe the photoinduced surface modulation at different stages of formation the exposure time was varied in the range 2.5 s to 250 s.

The photopolymer surface after recording was scanned using a white light interferometric (WLI) surface profiler *MicroXAM S/N 8038*.

The film thicknesses were characterised by cutting the photopolymer layer using a sharp scalpel and measuring the dimensions of the cut with the WLI profiler.

4. Results and discussion

4.1. Position of the surface relief peaks

In order to determine the position of the surface relief peaks holographic gratings with low spatial frequency of 2 l/mm were recorded in spin coated layers with thickness of 2 μm . The recording time was varied between 5 and 10 s and the recording intensity was between 10 and 30 mW/cm^2 . The sample surface was examined with a Dektak_3 profiler. The apparatus is equipped with a photcamera. This facilitates observation of the position of the measuring tip on the surface during the scan. The illuminated and non illuminated areas of the photopolymer surface are well distinguished as white

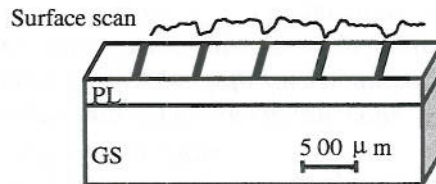


Fig.3 Position of the surface relief peaks when a simple diffraction grating with spatial frequency of 2 l/mm is recorded. Light illumination leads to well distinguished consecutive bleached and unbleached stripes. PL - photopolymer layer, GS - glass substrate

and pink stripes (Erythrosine B makes the unexposed photosensitive layers pink). The position of the tip with respect to the beached and unbleached fringes can be easily correlated to the measurement in vertical direction. The results from this measurement are presented in Fig.3. It was observed that the surface relief peaks appear in the areas where the light was absorbed. This is in agreement with the previous results from investigation of surface relief modulation in thick acrylamide photopolymer films after light exposure through a mask¹³. The observation of the surface relief peaks in the areas illuminated by light implies that the mass transport must be the main mechanism of surface relief formation. At the same time it is known¹⁴ that the free radical polymerization is usually accompanied by shrinkage of the material. Such shrinkage could be expected in holographic recording as well. If the surface relief modulation occurred due to photopolymer shrinkage only, the relief peaks would be observed in the dark fringe areas. It is possible that, in the beginning of the surface relief formation, the peaks are indeed positioned in the dark fringe areas and shortly after that, due to mass transport from the dark to bright fringe areas, these initial peaks disappear and new peaks grow in the bright fringes. The latter are observed during the scan with the Dektak_3 profiler. It should be kept in mind that the measurements of the surface relief modulation presented here are not real time measurements. With the present technique we can not observe what happens in the initial stage of surface relief formation. Although we varied the intensity and time of the recording in order to find exposure conditions at which the initial shrinkage will not yet be entirely compensated by diffusion, no surface relief peaks localized in the dark fringe areas were observed.

4.2. Dependence of the relief amplitude on the exposure level

In order to investigate the dependence of the surface relief amplitude on the level of exposure the photopolymer layers were illuminated for time intervals varied between a few seconds to a few hundreds of seconds. In all of the investigated samples the initial increase of the surface relief amplitude with exposure time was followed by a decrease. An example of this behaviour is given in Fig.4. The investigated 2 μm thick layer was prepared by gravity settling method. The measured dependences on the level of exposure reveal that there is an optimum exposure level for achieving maximum

surface relief amplitude. In order to understand the origin for this optimum exposure the intensity dependence of the surface relief amplitude was studied.

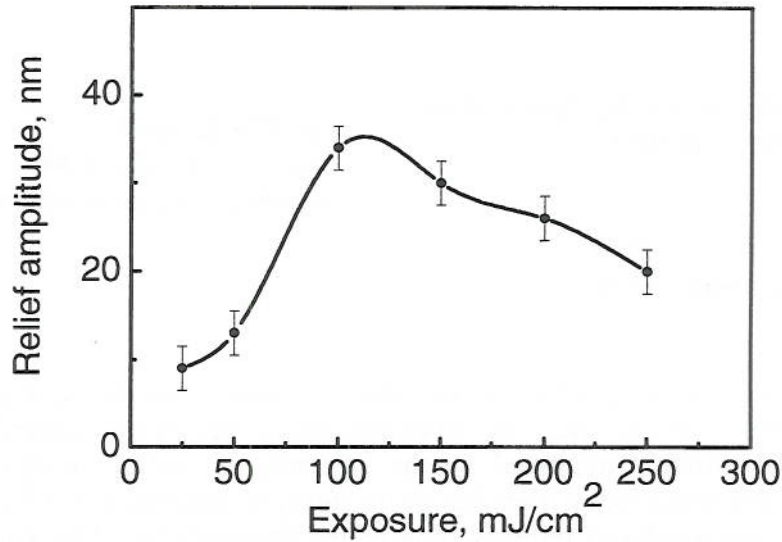


Fig. 4 Dependence of the photoinduced surface relief amplitude on the exposure level. The 2 μm thick sample was illuminated with intensity of $2.5\text{mW}/\text{cm}^2$ at spatial frequency of recording of 14 l/mm.

4.3. Dependence on the intensity of recording

The intensity dependence of the photoinduced surface relief amplitude in layers with constant thickness of 2 μm was studied. The results representing the intensity dependence of the surface relief amplitude inscribed in spin coated layers at 10 and 100 l/mm are shown in Fig. 5. At both spatial frequencies it was observed that illumination with higher intensity leads to a higher surface relief amplitude.

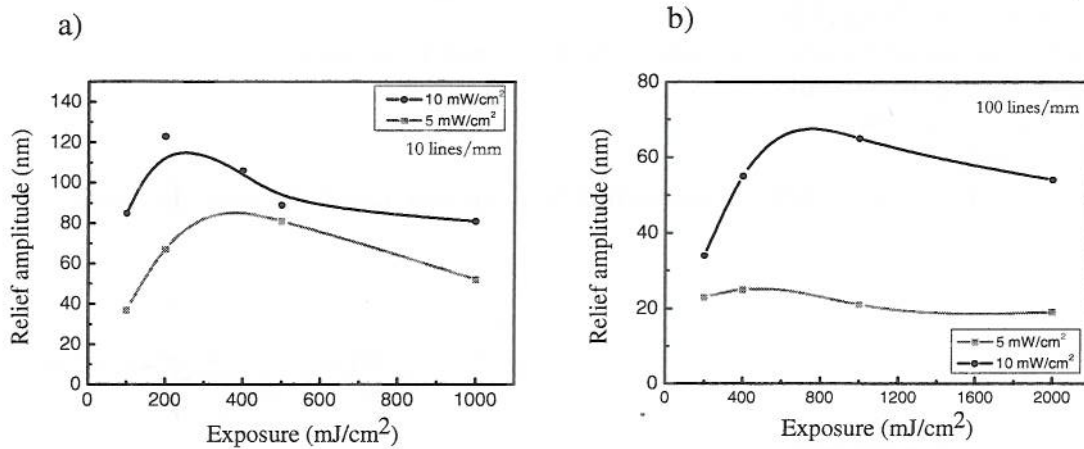


Fig. 5 Intensity dependence of surface relief amplitude in 2 μm spin coated layers at spatial frequency of recording of 10 l/mm a) and 100 l/mm b).

Similar intensity dependence of the photoinduced surface relief at 14 l/mm spatial frequency of recording was observed in 2 μm thin layers prepared by gravity settling method. At spatial frequency of 100 l/mm the difference between the two recording intensities was even more pronounced.

As the optical density of the layers is very small (in order of 0.01OD) the concentration of the photons absorbed will be low and the absorption of a single photon is expected to cause the same final number of monomer molecules polymerized and the same gradient in the monomer concentration, created at both 5 and 10 mW/cm^2 intensities of recording, when the same exposure levels are used. In this case the same final surface relief amplitudes would be expected if no additional factor plays a role during the recording. But if the diffusion of monomer is influenced by interaction between the photopolymer layer and the substrate then the actual number of diffusing molecules in unit time might become important in order to overcome the forces arising from the interaction with the substrate. At higher intensity the rate of delivery of the photons is faster and the number of diffusing molecules in unit time interval would be higher thus collectively overcoming the interaction with the substrate which would be expected to stop the diffusion.

The picture of the surface relief amplitude dependence on the intensity of recording completely changes when thicker layers were examined. The increase of layer thickness to 3.5 μm led to observation of an opposite dependence on the

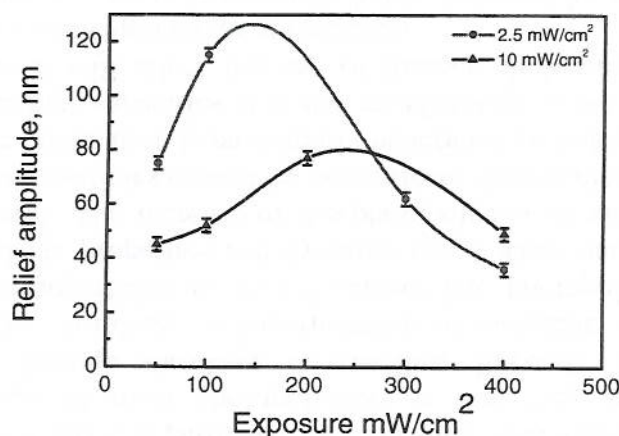


Fig. 6 Intensity dependence of surface relief amplitude in 3.5 μm layer prepared by gravity settling at spatial frequencies of 14 l/mm.

intensity. It is shown in Fig.6 that the recording with higher intensity at 14 l/mm resulted in lower surface relief amplitude. Similar dependence was observed in layers with thicknesses above 25 μm and it was explained by the ratio between the times required for the polymerisation and diffusion processes to occur. At low intensity the monomer molecules would have more time to diffuse into the bright fringes before being polymerized outside and thus to contribute to higher surface relief amplitudes. Also, at higher intensities, there is a tendency for larger numbers of short chain polymer molecules to form and these, being smaller, can more readily diffuse away from the bright fringe regions, leading to lower surface relief modulation. The results from the intensity dependence reveal that in the layers with different thicknesses the contribution of the diffusion process to the final surface relief modulation is different. Such dependence could be expected if the interaction of the substrate and the photopolymer material can not be neglected below a given thickness of the layer.

4.4. Dependence on thickness of the samples

The influence on the photopolymer layer thickness on the surface relief amplitude was studied in detail in layers prepared by gravity settling method. Layers with thicknesses from 1.7 to 4.5 μm were studied. The results from this investigation are shown in Fig.7. The layers were illuminated for 50 s with intensity of 5 mW/cm^2 at 8 and 14 l/mm spatial frequencies and with intensity 10 mW/cm^2 at spatial frequencies 70 l/mm and above. It is seen from Fig.7 that the increase of the photopolymer layer thickness leads to increase in the final surface relief modulation. This is especially

clear at lower spatial frequencies up to 90 l/mm. A linear dependence of relief modulation on layer thickness is to be expected here. As monomer diffuses in, the polymerising area swells, and the surface is forced upwards. Since the polymerized area extends through the depth of the layer, a thicker layer would be expected to produce a greater modulation at the surface. This supports the model describing the material diffusion as the main factor controlling the light induced surface relief modulation in this photopolymer system. When the spatial frequencies of recording approach 200 l/mm however the dependence of the surface relief amplitude on the layer thickness is not so pronounced anymore. This could be explained by the increased role of the surface tension at these higher spatial frequencies. It would be expected to prevent the surface from deformation and despite the fact that more swelling would be expected in thicker layers the overall surface relief amplitude would remain low and almost the same for all thicknesses.

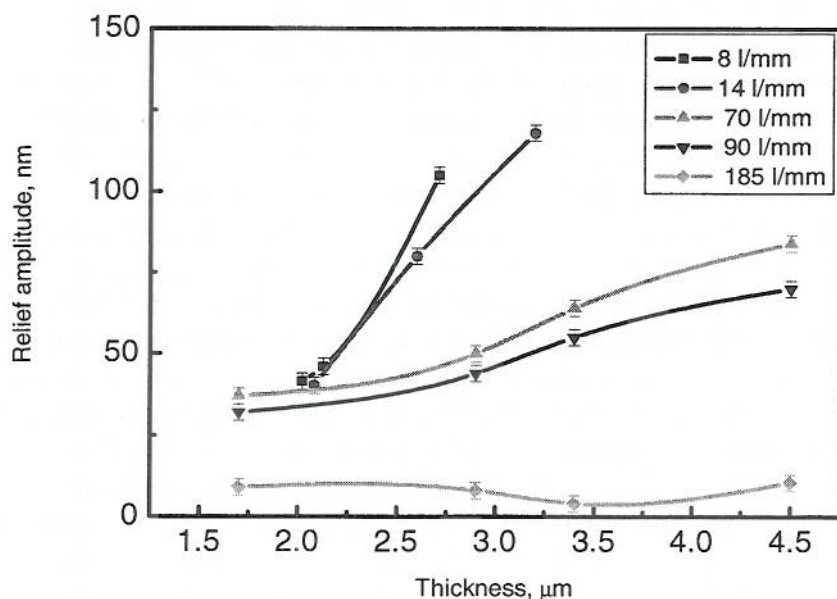


Fig. 7 Dependence of the surface relief amplitude on the photopolymer layer thickness. The layers are illuminated for 50 s with intensity of 5 mW/cm² at spatial frequencies of recording of 8 and 14 l/mm and with 10 mW/cm² when the recording frequencies are from 70 to 185 l/mm.

4.5. Spatial frequency dependence

Similar decrease of the final surface relief amplitude with spatial frequency increase was observed in the layers prepared by spin coating. The results are shown in Fig. 8. As for the layers prepared by gravity settling technique this decrease could be explained by the increased role of the surface tension. No decrease at lower spatial frequencies was detected for both types of layers. Such a decrease would be expected if the contribution of mass transport decreases when the fringe spacing increases. The fact that such low spatial frequency cut-off was not observed could be considered as evidence that the diffusion processes in this acrylamide based-photopolymer system are relatively fast when compared to other photopolymer systems. In other photopolymer systems, for example in the one reported by Smirnova¹² et. al, such low spatial frequency cut off is clearly observed.

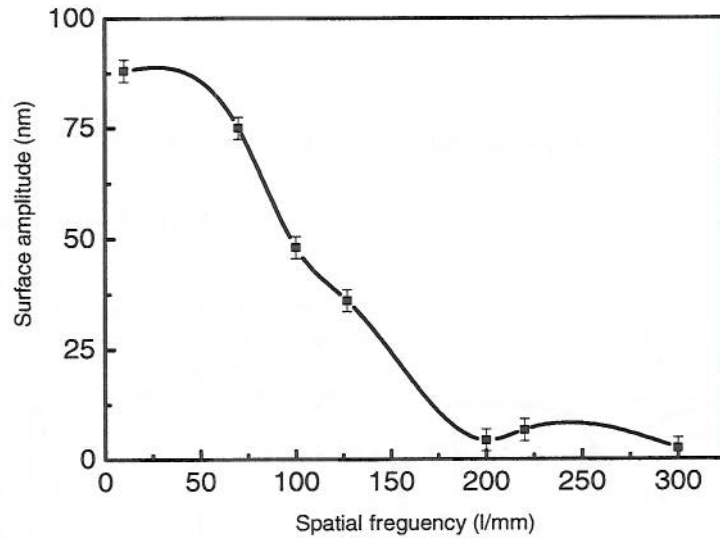


Fig.8 Spatial frequency dependence of the surface relief modulation in spin coated layers with thickness of 2 μm . The layers were illuminated for 100 s with intensity of 10 mW/cm^2 .

4.6. Holographic inscription of patterns

Patterns with different spatial frequency and profiles were inscribed in the thin photopolymer layers prepared by gravity settling method. Examples are shown in Figs. 9 -11.

The difference in the inscribed surface relief profile when the intensity of recording was changed from 2.5 to 10 mW/cm^2 at spatial frequency of recording of 14 l/mm can be observed in Fig. 9. It was demonstrated that by choosing the intensity

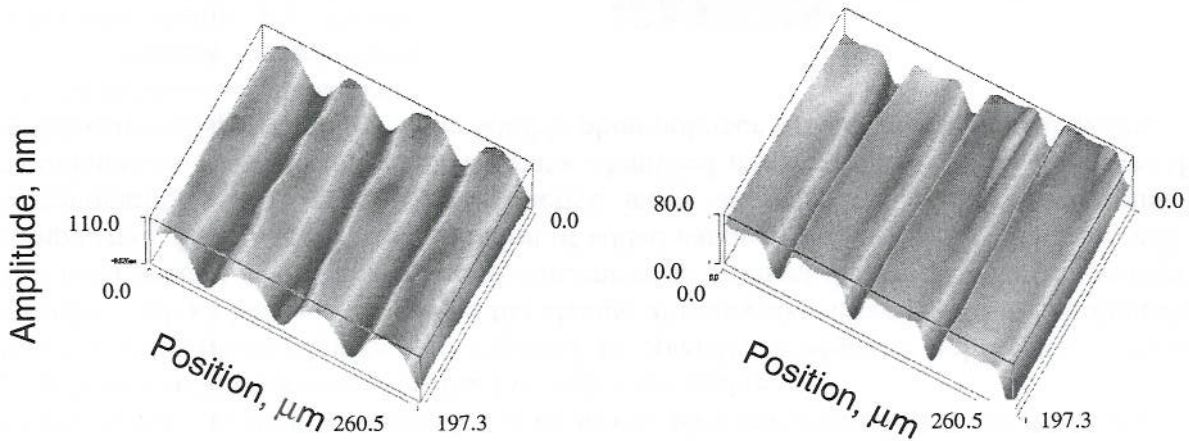


Fig. 9 Photoinduced surface relief modulation after illumination of 3.5 μm thick layer with 200 mJ/cm^2 exposure. Intensity of recording is 2.5 mW/cm^2 a) and 10 mW/cm^2 b).

and exposure time not only the amplitude but the shape of the photoinduced surface profile can be controlled. This could turn out to be an important feature when orientation of molecules with different size and shape is looked for. Patterns obtained after two consequent recordings between which the position of the sample has been changed are shown in Fig. 10 and Fig.11.

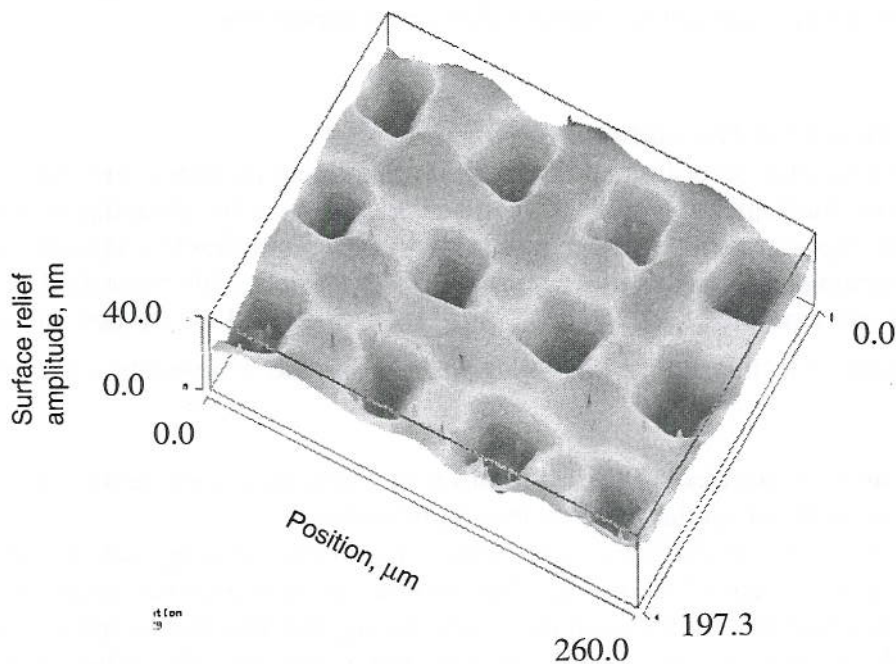


Fig.10 Photoinduced pattern inscribed after two consecutive holographic recordings at spatial frequency of 14 l/mm. Recording intensity is 2.5 mW/cm and the recording time is 10 s.

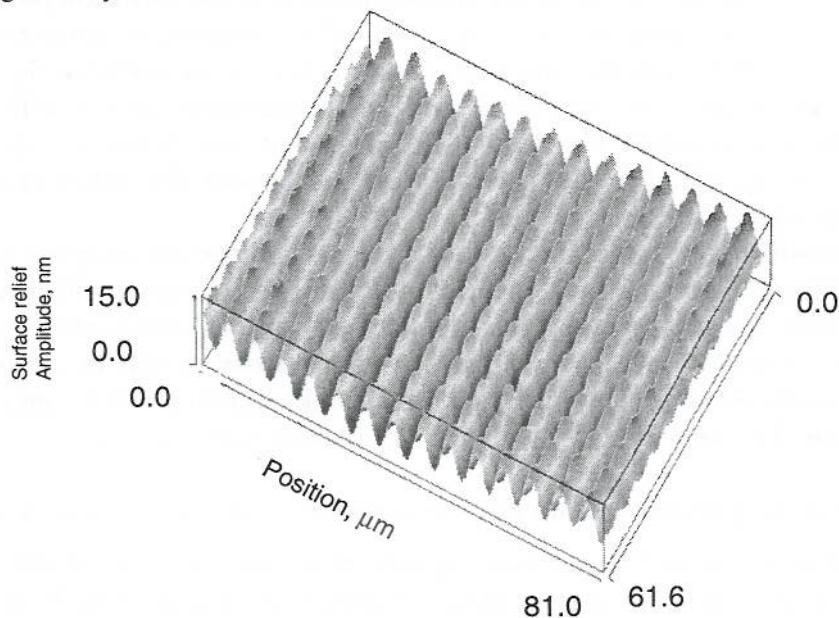


Fig.11 Photoinduced pattern inscribed after two consequent holographic recording at spatial frequency of 185 l/mm. Recording intensity is 10 mW/cm² and the recording time is 10 s.

Conclusions

The process of surface relief formation by holographic recording in thin acrylamide-based photopolymer layers was studied. It was established that the surface relief peaks coincide with the areas illuminated by light. This observation together with the measured dependencies of the surface relief amplitude on the intensity of recording, spatial frequency of recording and the layer thickness suggest that the diffusion of material plays a substantial role in the surface relief formation. It was shown that when the layers are a few micrometers thick their thickness becomes an important factor for the final surface relief amplitude and profile. This could be explained by an increased substrate-photopolymer layers interaction which slows down the diffusion processes. The dependence on the layers thickness is especially pronounced at low spatial frequencies. At higher spatial frequencies the overall surface relief amplitude decreases in all layers and the thickness dependence vanishes. At these spatial frequencies the surface tension possibly plays the major role by preserving the photopolymer layer surface from deformation.

During the course of this study it has been demonstrated that the surface relief amplitude and more importantly the profile shape can be controlled by the intensity of recording. This could appear to be an important feature for the application of this photopolymer system in the design of diffractive optical elements and liquid crystal devices.

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