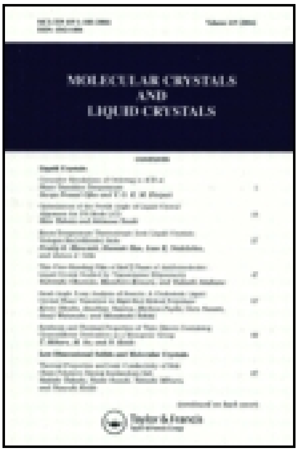

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N. D. Vorzobova [a], V. G. Bulakova [a], N. M. Kalinina [a] & Yu. E. Burunkova [a]

[a] Saint-Petersburg State University of Information Technologies, Mechanics and Optics, Saint-Petersburg, Russia

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Regularities in the Formation of Microstructural Elements in a Light-Curable Nanocomposite

N. D. VORZOBOVA, V. G. BULAKOVA, N. M. KALININA, AND YU. E. BURUNKOVA

Saint-Petersburg State University of Information Technologies, Mechanics and Optics, Saint-Petersburg, Russia

The regularities of microstructural elements formation in UV-curable nanocomposite by deep and interference lithography methods have been studied. The dependency of dimensional characteristics of microstructural elements on the amplitude mask parameters, exposure level, layers thickness has been established. The ways to reduce characteristic sizes of microstructural elements and to increase an aspect ratio have been obtained. A possibility to realize an interference method has been shown and diffraction characteristics of the structures determined.

Keywords Aspect ratio; characteristic size; deep lithography; interference lithography; nanocomposite; photopolymerisation; polymeric microstructure

Introduction

The development of methods and technologies of three-dimensional polymeric microstructural elements fabrication is relevant for various spheres of science and technology, such as electronics, communications, micromechanics, medicine, biology, information and laser engineering, chemistry, instrument making. Such elements are in demand as elements of photonics, optical integrated microchips, a microcomponent of MEMS and MOEMS, biochips, catalysts, physical value microsensors.

One of possible methods of three-dimensional microstructural elements fabrications is a deep lithography [1–5]. The current level of research in this sphere is characterized by a search for promising materials, radiation sources, a process of obtaining microstructural elements, and also of their possible configurations when reducing characteristic sizes of elements and increasing an aspect ratio. The best results are ensured by processes using X-ray and ion beams as exposing radiation, and high-level UV radiation [1–3]. A possibility to obtain elements with a high aspect ratio (height/width ratio) using X-ray and other short-wave radiation is determined as result their small angular spreading in matter. Installations based on such radiation sources, however, are costly and require compliance with safety measures,

Address correspondence to N. D. Vorzobova, Saint-Petersburg State University of Information Technologies, Mechanics and Optics, Kronverksky pr. 49, Saint-Petersburg, Russia. E-mail: vorzobova@mail.ifmo.ru

and the technologies cannot be used for large-scale production of cheap components. In this connection, the transition to processes using optical radiation, including soft UV radiation is relevant. The basic material used is negative photoresist SU-8 [4,5]. An important problem of this material using is a problem of removing residual solvent when applying thick layers. With the increase in layer thickness the removal of residual solvent is impeded by its slow diffusion through a polymer layer and possible only during high-temperature treatment. The complete of removal solvent from a layer of hundreds microns thick is problematic. The presence of residual solvent considerably worsens the quality of microstructural elements [4]. Thus, orientation toward materials ruling out the presence of solvent is relevant.

In there recent years new photopolymeric materials based on compositions of liquid monomers [6,7] have been developed, which do not require the use of solvents for application of layers. In order to viscosity increase, which is necessary for application of thick layers to obtain microstructures with a high height/width ratio, we have developed photopolymeric compositions based on acrylic monomers with an embedding of inorganic nanoparticles [8]. A mechanism of microelements formation in such materials is fundamentally different from the one in photoresist. It is based on radical photopolymerization in the presence of an initiator, in the result of which solid polymer is formed under the effect of radiation. A large positive changing of the refractive index in the material during photopolymerization process lead to light self-focusing effects and as result to compensation of initial spreading of optical radiation. The regularities of photopolymerization during self-focusing were in most detail studied as applied to the problem of the microelements formation at the optical fiber edge [9,10]. The works [10,11] show that in the result of self-focusing it is possible to obtain structures with a high aspect ratio by using long-wave radiation with high spreading.

This work, in continuation of the earlier ones, studies the regularities of three-dimensional microstructures formation by methods of deep and interference lithography in a nanomodified composition based on the acrylic monomers, the factors determining size characteristics of microstructural elements, possibilities to reduce characteristic sizes of elements and to increase an aspect ratio.

Conditions of an Experiment

The research was done using a new light-curable material – the nanomodified composition based on the mixture of acrylic monomers with embedding of ZnO nanoparticles, described in the work [8]. In order to viscosity increase the concentration of nanoparticles was increased to 12 weight percent. Microstructures were formed by a contact method [11] by matching of amplitude mask. The layer of liquid composition applied onto a glass support. The layer thickness was determined by the sizes of inlays and varied from 30 to 300 μm. An amplitude mask (mask plate) was manufactured by reducing (20^x) an initial pattern prepared on a computer. The density of the amplitude mask varied from 0.5 to 2.5. As a configuration under research, a line art test was used with changing of the elements sizes (line widths) and distances between them. The elements sizes were given in a micron range with a view to investigating of size characteristics by optical methods. The exposure was by UV radiation with wavelength of 365 nm. Uncured material was removed when treating with isopropyl alcohol. The heights of microstructural elements and their transverse dimensions (widths) were measured using micro interferometer MII-4.

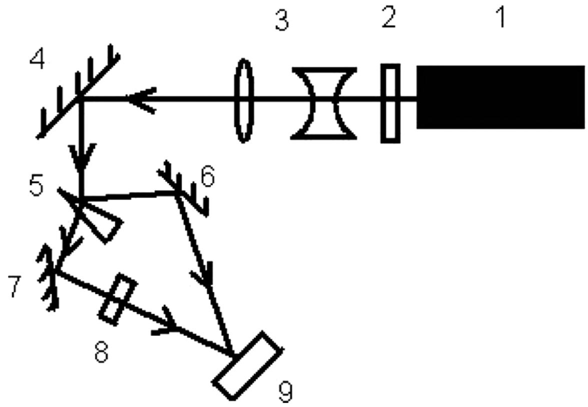


Figure 1. Experimental setup scheme. 1-helium-cadmium laser, 2, 8-light filters, 3-quartz telescope, 4, 6, 7-mirrors, 5-quartz wedge, 9-recording material.

An interference method was realized recording of interference structure formed in the interaction of two plane waves (Fig. 1) at the wavelength of 325 nm (radiation of a helium-cadmium laser GKL-40 I).

The angle between the interfering beams amounted to 10° in order to obtain structures in a micron range of sizes to allow an express evaluation of the structures quality by optical microscopy methods. A quantitative evaluation of the structures was conducted by a diffraction method during measuring the intensity of a diffracted beam in the first order of diffraction at the wavelength of 633 nm and the intensity of a dispersion halo, and also by a method of optical microscopy (using a laboratory microscope Labomed-3).

Experimental Results and Discussion

The investigation of a dependency of microstructural elements height on the exposure (Fig. 2) has shown that already at an initial stage of the photopolymerization process (with exposure duration of up to 10 sec) 50–70% of the final height of the microstructure is formed.

The growth kinetic of the microstructural elements heights is qualitatively similar to the growth kinetic of the polymeric layer thickness in macrovolume (without mask matching). However, the regularities of photopolymerization in microvolume have differences. Thus, rate of heights growth of microelements depend on the line width in the amplitude mask and reduce with its reduction. The height of the microstructural elements does not practically depend on the distance between the elements and the density of the mask.

The investigation of the width growth kinetics of the microstructural elements has determined the difference from the height growth kinetics. Thus, the percentage relation of the initial width (for exposure duration up to 10 sec) to the final width is less than the corresponding relation for the heights of the microstructures. The initial width of the elements considerably depends on the line width in a mask plate, the distance between the lines, and the mask density and can be considerably less (from 5%) than the final width (Fig. 3).

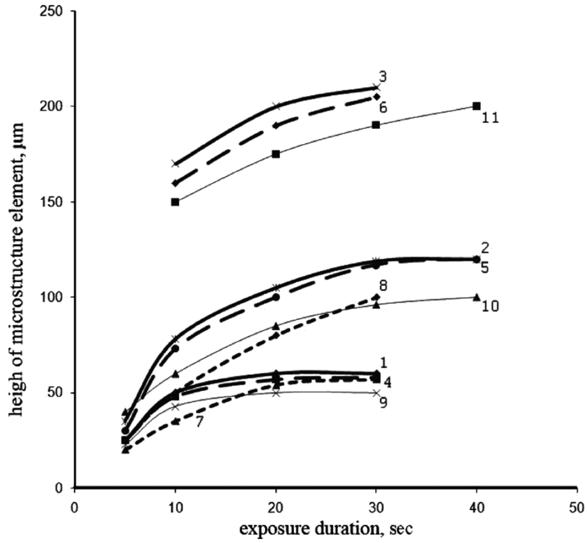
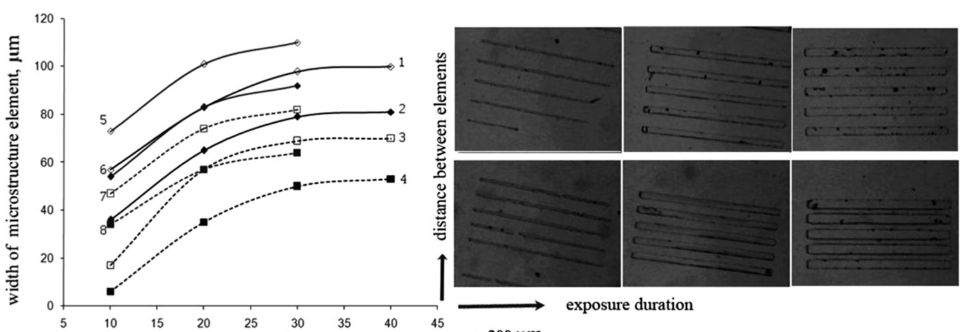


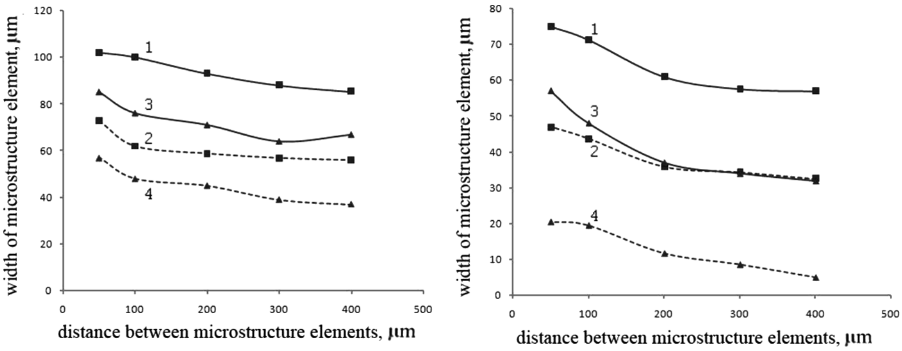
Figure 2. Dependency of the microstructural elements height on the exposure duration. Line width in an amplitude mask: 100 µm (1, 2, 3), 75 µm (4, 5, 6), 50 µm (7, 8). 9, 10, 11 – are the growth kinetics of a polymeric layer. Layer thickness: 30 µm (1, 4, 7, 9), 100 µm (2, 5, 8, 10), 300 µm (3, 6, 11).

The rate of width growth of the elements does not practically depend on the line width in an amplitude mask, but increases with the reduction in the distance/width ratio. The element width (Fig. 4) considerably depends on the distance between the lines (reduces with its increase) and the mask density (increases with the decreasing of density) and can be less than the given line width in the amplitude mask. The width growth kinetics of the elements and their final transverse dimensions are independent of the layer thickness, which gives evidence to the formation of elements with almost vertical walls. The analysis of the kinetics of the elements formation during exposure through an amplitude slot mask has shown that the elements



(a) (b)

Figure 3. Dependency of a microstructural elements width on the exposure duration. Mask density 2.5 (1, 2, 3, 4) and 1.2 (5, 6, 7, 8). Line width: 100 µm (1, 2, 5, 6) and 75 µm (3, 4, 7, 8). Distance/width ratio: 4 (2, 4, 6, 8) and 0.5 (1, 3, 5, 7). Layer thickness 100 µm.



(a) (b)

Figure 4. Dependency of the microstructural elements width on the distance between the elements. Line width: 100 μm (a) and 75 μm (b). Plate density: 1.2 (1, 2) and 2.5 (3, 4). Exposure duration: 10 sec (2, 4) and 20 sec (1, 3).

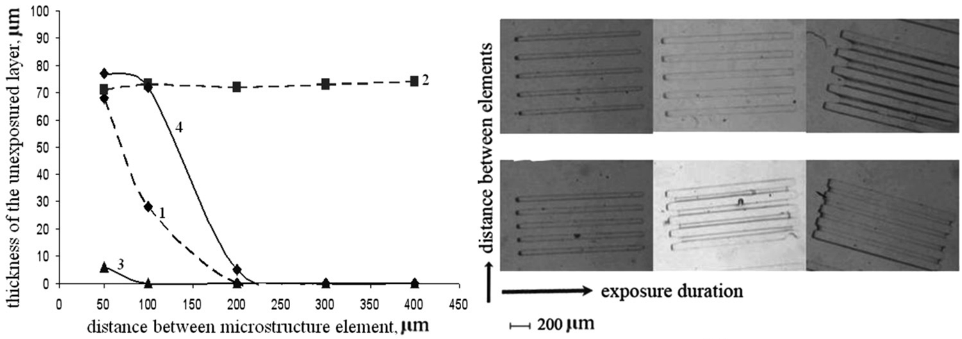
formation begins with the formation of a solidified area by the center of the exposing beam with considerable longitudinal and small transverse dimensions. With the subsequent increase in the exposure the transverse dimensions grow.

The formation of elements with small transverse dimensions at the initial stage of photopolymerization process when the height was considerable and a reduction in the transverse dimensions (in relation to the sizes given in the amplitude mask) when the distance between the elements increases, is a positive factor, both in terms of a reduction in the characteristic sizes of the polymeric elements, and in terms of an increase in the aspect ratio.

The observed reduction in the transverse dimensions of the microstructural elements when the distance between the elements increases can be related with inhibition of the photopolymerization process by oxygen in air [6,10]. When the distance between the exposure areas increases as a result of an increase in oxygen content in the adjacent areas of the material and its diffusion into the exposure area, the photopolymerization process slows down, and the element is narrowed.

Of a great scientific and practical interest is the issue of confluence of elements located close to each other. The research determined the following regularities. The confluence of the microstructural elements takes place as a result of a polymeric layer formation under the dark areas of the amplitude mask. The thickness of the unexposed polymeric layer between the elements of the microstructure increases when the distance between them decreases, the exposure increases, and the mask density decreases (Fig. 5). Photopolymerization under the dark areas of the amplitude mask is observed even by greater densities (over 2.5), i.e., with exposures considerably less then the photopolymerization threshold.

Mechanisms determining the confluence of located close to each other elements are studied not enough. On the basis of the available perceptions it can be assumed that the degree of photopolymerization in the interstices between the elements can be determined as a superposition of three processes: oxygen inhibition [6,10], shrinkage of light-curable composition [7], and also diffusion of photoradicals that is supposed in the work [12]. In the result of these processes when the distance between the elements reduces, it is probable that more favorable conditions are formed for



(a) (b)

Figure 5. Dependency of the thickness of the unexposured polymeric layer on the distance between the elements. Mask density: 1.2 (1, 2) and 2.5 (3, 4). Exposure duration: 20 sec (1, 3) and 40 sec (2, 4). Layer thickness 100 µm. Line width 100 µm.

photopolymerization in the interstices between them – a reduction in oxygen amounts, a reduction in the layer thickness due to shrinkage and, probably, an increase in the concentration of free radicals.

In order to reduce the characteristic sizes of elements of polymeric structures a possibility to realize an interference method has been investigated. The first samples of periodic structures have been obtained and their diffraction characteristics determined. Figure 6 shows dependency of the diffraction efficiency and light diffusion obtained in a light-curable nanocomposite (BisA/2Carb, 7/3, with nanoparticles of ZnO −12% [8]) on the exposure time for the given layer thickness 20 µm.

For the recorded structures high diffraction efficiencies are obtained jointly with high light diffusion. The following causes leading to high light diffusion were supposed to be possible: an incomplete washout of uncured material and confluence of the elements of a structure. The influence of the duration of treatment in isopropyl alcohol on the characteristics of the structures has been studied. The following

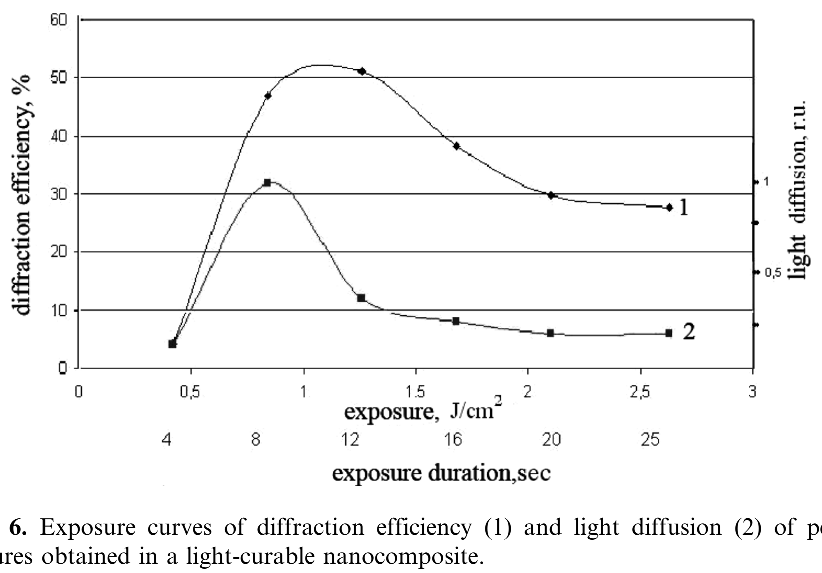
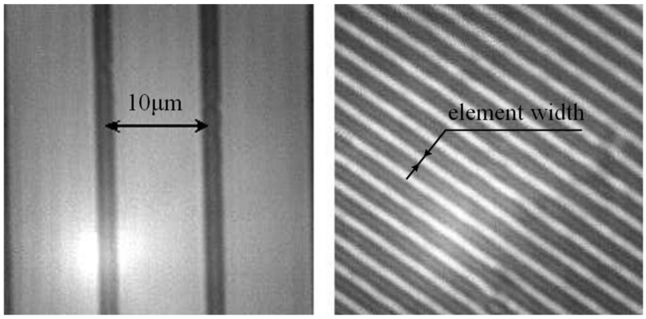


Figure 6. Exposure curves of diffraction efficiency (1) and light diffusion (2) of periodic structures obtained in a light-curable nanocomposite.



(a) (b)

Figure 7. Appearance of a structure obtained by an interference method. a – image of the stage micrometer, b – image of the structure.

regularities have been determined: a tendency of diffraction efficiency increasing by duration of development increasing without a considerable reducing in light diffusion; a non-monotonic dependency of light diffusion on the development time; an increase in the optimal treatment duration (up to 30 min) in relation to that by microstructural elements obtaining by a contact method (10 min).

Evaluations of the structural elements sizes (in comparison with an image of a stage micrometer) made using an optical microscope have shown that the size of elements is 1 μm, which corresponds to the size calculated with the use of the Bragg condition (Fig. 7).

The object of further research is an investigation of the dimensional features of periodic structures and the factors determining them during an increase in frequency and layer thickness.

Conclusions

The regularities of three-dimensional microstructures formation on new material-nanomodified composition based on acrylic monomers have been investigated by deep and interference lithography methods. A dependence of microstructures elements dimensional characteristics on exposure parameters, amplitude mask characteristics (optical density, lines width and distance between them) and layer thickness have been determined. A peculiarity of the elements growth kinetics such as preferential height growth at the initial stage of the process with small transverse dimensions determining a possibility of elements characteristic sizes decreasing and the aspect ratio increasing has been revealed. It was shown that the element width considerably depends on the distance between the elements (reduces with its increase) and can be less than the given line width in the amplitude mask. A possible mechanism of this regularity was discussed. A possibility of the formation periodic structures with diffraction efficiency 50% by interference lithography method has been shown. The results are of interest for fabrication of polymeric structures using deep and interference lithography methods.

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