Laser technologies for three-dimensional polymeric structures fabrication

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Abstract. The processes of formation volume polymeric structures with periodic and arbitrary three-dimensional configuration and optical properties of the elements on their basis are described.

Laser technologies for three-dimensional polymeric structures are an issue of wide research. These technologies include, in particular, laser interference lithography (LIL), which allow a periodic structure formation in the interference light field. Most of research is based on the use of various types of photoresists including a photoresist SU-8 [1-3]. The main problem of the use of this material when the thickness of the layer is large is the problem of residual solvent removing. This paper discusses the processes of three-dimensional structures formation in photopolymerized acrylate compositions and nanocomposites [4, 5] excluding this problem. Along with the possibility of the relief structures formation by interference lithography, processes based on holographic methods are also considered.

When implementing the method LIL structure are formed when exposed in interference field, and followed washing in isopropanol to remove the uncured phase. Depending of the quality of the structures on the exposure parameters established the possibility of relief structures obtaining only for small exposures. Increase in the exposure leads to the formation of bridges (Fig.1b), and then the processes of mass transfer take place and the structures formed are based on the nanoparticles distribution. Possibility of nanoparticles transport in the nanocomposite materials was considered in a number of papers [6-8]. On the photo (Fig.1g) in a cut of structure can be seen nanoparticles (zinc oxide) in the gaps between the polymeric elements.

Figure 1. Kinetics of formation of the periodic structure. Power density of 8 mW/cm². Wavelength of the recording light is 325 nm. Period is 6 microns. Exposure Duration 2 (a), 4 (b), 8 (c), 20 (d) s.

Also, process for structures fabrication with a refractive index modulation formed as a result of mass transfer in interference field was investigated. The process for obtaining the structure consists of two stages - the exposure in interference field and the post-exposure UV illumination (without chemical treatment). The dependence of the diffraction properties of periodic structures in the nanocomposite with silica nanoparticles (with a size of 14 nm and 7 nm) on the frequency of the interference field, layer thickness, exposure parameters was investigated. The possibility of obtaining high refractive structures with a diffraction efficiency of 80% at a layer with thickness of 100 microns
and a frequency of 300-400 mm\(^{-1}\) was found. Increasing in the frequency leads to a decrease in diffraction efficiency. By increasing the layer thickness an increase in light scattering is observed. Thus the scattering elongated in a direction perpendicular to the diffraction plane as a result the selective properties of the Bragg grating. Examination of cross-sections of structures obtained on a microtome showed that the structures are formed in the all thickness of the layer and the structures are volume (Fig. 2a). Fig. 2b shows the results of measurements of the angular selectivity of the structures with different periods.

![Image](image_url)

**Figure 2.** The cut of structure (a), angular selectivity of volume periodic structures (b).

In addition to the one-dimensional structures structure at multi beams interference (Fig. 3c) were obtained. The structures were formed in the layers of composition with a thickness of 100 microns deposited on a glass or film substrates.

![Image](image_url)

**Figure 3.** The diffractive element based on volume structure (a) view of the structure obtained by four-beam interference (c) and the diffraction patterns (b, d).
Results given above were obtained when recording with continuous radiation at a wavelength of 442 nm. We investigated also the possibility of pulsed radiation using with a wavelength of 532 nm and the dependence of the diffraction properties of the structures of the pulse frequency and pulse energy. The structures were formed with a period up 3 microns. The highest diffraction efficiency - 74% is obtained at a frequency of 10 Hz and a pulse energy 2mJ and is comparable with that obtained at a given wavelength when recording with continuous radiation.

It was researched the possibility of a three-dimensional polymeric elements forming with the by projection to the volume of photopolymerized material of three-dimensional intensity of the laser radiation distribution formed by hologram. The main problem of the implementation of this approach is to display the configuration of the projected wavefront in the material volume. Solution was achieved as a result of oxygen inhibiting the polymerization process and the corresponding radiation absorption in layer. The holographic image of model objects with flat, spherical, sloped and stepped surfaces was projected in the volume of the photopolymerized photocurable composition. On Fig. 4 present a view of the three-dimensional polymeric elements that were obtained as a result displaying of the wave front configuration.

The elements are formed as a result of one light action what determines the advantage of the proposed method relatively the widely used technologies of laser stereolithography or 3D printing [9, 10] which to obtain similar object require a significantly longer time.

The results can be used to obtain, diffractive elements, the elements for light beams forming, elements with arbitrary three-dimensional surface, elements of the photonics with high performance characteristics - optical transparency, high heat resistance and light moisture when simplicity and low cost of processes for their formation

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