Fabrication of Scaffolds and Micro-Lenses Array in a Negative Photopolymer SZ2080 by Multi-Photon Polymerization and Four-Femtosecond-Beam Interference

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Abstract

Multi-photon polymerization using interference of several laser beams is a promising technique for mass fabrication of 3D periodic micro-structures over large areas, which can be used in micro-biology (artificial scaffolds), photonics (photonic crystals), micro-optics (micro-lenses). While the direct laser writing (DLW) approach is a relatively slow process, use of the interference field can be a significantly faster alternative route of parallel processing when periodic structures are produced by a single laser exposure. We present examples of scaffolds and micro-lens arrays fabricated over a large area by multi-photon polymerization in a negative ultra low shrinkage and biocompatible photopolymer SZ2080 (ORMOSIL) using four-beam interference of a femtosecond laser.

Keywords: Multi-photon polymerization; four-beam interference; femtosecond laser; periodic microstructures; microlenses array; SZ2080; Ormosil

1. Motivation

Multi-photon polymerization (MPP) based on the laser direct writing is a powerful technology to generate three-dimensional (3D) micro-structures with a high resolution, but fabrication using this technique is time consuming and hardly acceptable for the real industrial batch production even when the sample size is only 100 x 100 microns large [1]. Solution of the problem can be use of the laser beam interference. Fabrication of periodic micro-structures by interference of several laser beams over a large area is much faster than fabrication by the laser direct writing technique. Using the laser beam interference it is possible to get periodic structures by a single laser exposure whereas by the laser direct writing technique only one voxel (volumetric pixel) is fabricated by the single laser exposure.

MPP by interference is a very attractive and promising technique for mass fabrication of the functional devices for practical applications due to possibility of relatively rapid fabrication over a large area of periodic micro-structures. These periodic micro-structures could be used as artificial scaffolds which enable controlling the stem
cell proliferation and differentiation sequenced by advances in tissue engineering and regenerative medicine [2, 3]. Cells in a living organism are surrounded by an extracellular matrix which plays an important role in cell functioning, proliferation, differentiation, adsorption, etc. The extracellular matrix forms natural scaffolds for every tissue. At this point, studies are focused on producing artificial scaffolds out of biocompatible materials. Such scaffolds could act as a skeleton for controllable stem cell growth and formation of artificial tissues [4].

In this study we present our results of using the MPP by interference technique not only in fabrication of artificial scaffolds but also more complex devices such as micro-lenses. Using this technique, 2D array of micro-lenses was produced by a single laser exposure. Precise control of positioning enabled us to fabricate micro-lenses arrays over a large area relatively fast. The fabricated components can be used for practical applications such as: fiber coupling and optical switching, collimation of lasers diodes, imaging systems and sensors, beam homogenizers for lasers and illumination systems, array optics featuring high precision, etc. [5].

2. Experimental setup

Experimentally polymerization using the four-beam interference was realized using an experimental setup shown in Fig. 1.

![Experimental setup of multi-photon polymerization by four-beam interference (for details see text below); (b) enlarged fragment of the optical setup (4F imaging system).](image)

**Fig. 1.** (a) Experimental setup of multi-photon polymerization by four-beam interference (for details see text below); (b) enlarged fragment of the optical setup (4F imaging system).

Experimental setup included: a femtosecond laser Pharos (1030 nm, ~290 fs, 6 W, 200 kHz, Light Conversion Ltd.), a diffractive optical element [6] (DOE, MS0202, HoloOr Ltd.), two lenses (L1 and L2) with focal lengths of F1 and F2, positioning system XYZ, diaphragm (D) and a few holding mirrors (M1, M2, M3, M4). The laser beam in the experimental system was controlled with the electro-optical shutter. DOE was used to split the laser beam into four equal beams. The diaphragm was used to block undesirable beams that appear after splitting the laser beam by DOE. Energy of the laser was tuned directly from the laser control board. We used a commercial hybrid organic-inorganic Zr-containing negative photopolymer SZ2080 (chemical formula C₄H₁₂SiZrO₂) [7] (FORTH, Greece) with 1% and 2% concentration of photoinitiator 4,4’-bis(dimethylamino)benzophenone.

3. Results and Discussion

Interference of four beams symmetrically arranged relative to a workpiece surface provides periodically distributed maxima of laser intensity and the pattern is preserved over the whole overlap area in normal direction. Applying such interference field of the ultra-short-pulse laser to the photopolymer, we initiate multi-photon polymerization at the interference maxima. The resulting structure is a 2D array of pillars whose height is limited by the thickness of the photopolymer. The period between pillars depends on the focal length of used lenses in the experimental system. By changing the focal length of lenses it is possible to fabricate pillar array with different periods. Relation between the period of four-beam-interference pattern and the focal length of lenses can be expressed as:
where \( \lambda \) is the period of four-beam interference pattern; \( d \) is the grating period of DOE; \( F_1 \) is the focal length of the first lens in experimental setup and \( F_2 \) is the focal length of the second lens in experimental setup (Fig. 1).

The grating period of the used DOE was \( 30 \mu m \). When the focal length \( F_1 \) of the lens L1 was \( 50 \text{ mm} \) and the focal length \( F_2 \) of the second lens L2 was \( 25 \text{ mm} \) (Fig. 1(b)), the period of four-beam interference pattern \( \Lambda \) estimated from (1) was \( 7.5 \mu m \). When lenses were exchanged (L2 with focal length of \( 50 \text{ mm} \), and accordingly L1 with focal length of \( 25 \text{ mm} \)), then the period of four-beam interference pattern \( \Lambda \) estimated from (1) increased four times and was equal to \( 30 \mu m \). The theoretical value of the period of interference pattern which was calculated by (1) matches the practically obtained pillar period (see Fig. 2). The smallest theoretical pillar period which could be fabricated is limited by diffraction and is equal to a half of the used laser wavelength (\( \lambda_{\text{laser}}/2 \)). The largest and smallest pillar period which could be fabricated by our experimental setup is limited by setup parameters, such as clear aperture of the lenses and separation angle between diffracted beams. Fabrication of pillars with a large period is also limited by power of the laser, because by increasing the period of pillars the radius of the overlapping area is increasing and it means that the intensity in the overlapping area is decreasing (see Table 1). The largest theoretical pillar period for used experimental setup (DOE separation angle - 2 deg, clear aperture of lenses - 20 mm, beam diameter on DOE - \( \sim 0.5 \text{ mm} \), focal length of one lens - \( 25 \text{ mm} \), focal length of the second lens is chosen considering to limit of the experimental setup) should be about \( 300 \mu m \) and the smallest - \( \sim 1.3 \mu m \). While the theoretical smallest period should be equal to half of the used laser wavelength, but this extreme period is difficult to fulfill experimentally due to large angle \( (180 \text{ deg}) \) between interfering beams. The smaller period than \( 1.3 \mu m \) could be realized by using shorter wavelength of interfering beams and different beam collecting systems.

The area which can be processed by a single laser exposure is equal to the beam overlapping area. It depends on the beam which incident into DOE diameter, on focal length of the used lenses, on laser exposure time and also how accurately the experimental setup is adjusted. The area experimentally processed by the single laser exposure was equal to \( \sim 920 \mu m \times 900 \mu m \) (Fig. 2 (a)) when average power was \( \sim 1.4 \text{ W} \), repetition rate - 5 kHz, exposure time - 5 min and period of the structure - \( 30 \mu m \). In this case peak pulse intensity was \( \sim 3.8 \text{ GW/cm}^2 \) (energy density - \( \sim 1.14 \text{ J/cm}^2 \)). By fabricating structures with the period of \( 7.5 \mu m \) with the average power \( \sim 820 \text{ mW} \), repetition rate - 20 kHz and exposure time - 4 s, the processed area was about \( 140 \mu m \times 130 \mu m \) (Fig. 2(b)). In this case peak pulse intensity was equal \( \sim 0.6 \text{ GW/cm}^2 \) (energy density - \( \sim 0.17 \text{ J/cm}^2 \)).

![Fig. 2. Examples of processed area by a single laser exposure. Process parameters: (a) average power - \( \sim 1.4 \text{ W} \), repetition rate - 5 kHz, exposure time - 5 min and period of periodic structure - \( 30 \mu m \); (b) average laser power - \( \sim 820 \text{ mW} \), repetition rate - 20 kHz, exposure time - 4 s and period of periodic structure – \( 7.5 \mu m \). Insets show the size of processed area in x and y direction.](image-url)
The relation between focal lengths of used lenses in experimental setup and radius of processed area by the single laser exposure can be expressed as:

\[ \frac{F_2}{F_1} = \frac{r_2}{r_1}, \]  

(2)

where \( F_2 \) and \( F_1 \) are the focal lengths of lenses; \( r_2 \) is the radius of the beams overlapping area; \( r_1 \) is the radius of an initial beam before the DOE.

By inserting (2) into (1), the relation between the period of fabricated structure and ratio of the overlapping area radius and the initial beam radius can be obtained.

\[ \frac{r_2}{r_1} = 2 \frac{\Lambda}{d}, \]  

(3)

According to (3) the radius of the processed area should be increased four times when the period of fabricated structure is increased from 7.5 \( \mu \)m to 30 \( \mu \)m. Experimental results in Fig. 2 demonstrate that the radius of the processed area increased more than 4 times. This discrepancy appeared due to the Gaussian spatial profile of the laser beam with higher intensity in the center. When laser exposure time was very short for the small-period structure, the polymerization reactions proceeded only in the center of the beam overlapping area where the laser intensity was higher than polymerization threshold. Fig. 3 illustrates variation of the processed area radius versus the laser exposure time. Structures which were fabricated by changing only laser exposure time (for the first structure it was 0.1 s, for the second - 0.5 s, for the third - 5 s) and other laser parameters were kept the same (average power - ~790 mW and repetition rate – 20 kHz) are depicted in Fig. 3.

![Fig. 3. Change in radius of processed area depending on the laser exposure times (0.1 s, 0.5 s, 5 s). Laser average power ~790 mW, repetition rate – 20 kHz.](image)

The ratio of intensities in the beam overlapping area and in the initial beam can be expressed as follows:

\[ \frac{I_2}{I_1} = \left( \frac{r_1}{r_2} \right)^2. \]

(4)

where \( I_2 \) is the intensity in the beams overlapping area; \( I_1 \) is the initial beam intensity before the DOE; \( r_2 \) is the radius of beams overlapping area; \( r_1 \) is the radius of initial beam before the DOE.

The relation between the period of fabricated structure and ratio of intensity in the overlapping area and the initial beam intensity can be expressed as:
\[ \frac{I_2}{I_1} = \left( \frac{d}{2A} \right)^2, \tag{5} \]

By using (3) and (5) equations it is possible to estimate the change of the initial beam radius and intensity in the beam overlapping area for different periods of the periodic structure (Table 1). Results in Table 1 show that by increasing the period of the periodic structure, radius of the processed area by a single laser exposure is also increasing, but laser intensity in this area decreases. For a period of 300 µm, the intensity in the beam overlapping area decreases 400 times compared to the initial beam intensity. This means that high-pulse-energy lasers are required in order to achieve the polymerization threshold and fabricate periodic structures with a large period by a single laser exposure.

Table 1. Dependence between the period of the structure (A, µm) and ratios of radius and intensities of the beam overlapping area (r₂ and I₂) and of the initial beam before the DOE (r₁ and I₁).

| Period of structure (A, µm) | Radius ratio (r₂/r₁) | Intensity ratio (I₂/I₁) |
|-----------------------------|----------------------|------------------------|
| 1.3                         | 0.087                | 133.14                 |
| 7.5                         | 0.500                | 4.0000                 |
| 30                          | 2.000                | 0.2500                 |
| 50                          | 3.333                | 0.0900                 |
| 100                         | 6.667                | 0.0225                 |
| 200                         | 13.33                | 0.0056                 |
| 300                         | 20.00                | 0.0025                 |

Examples of fabricated structures by a single laser exposure are shown in Fig. 4. Laser parameters for fabricated pillar array in Fig. 4(b) and Fig. 4(c), accordingly, were: average power ~0.4 W and ~1.5 W, repetition rate ~ 20 kHz and 5 kHz, exposure time ~ 1 s (20000 pulses) and 5 min (1.5×10⁶ pulses). The period of fabricated structures in Fig. 4(b) and Fig. 4(c) respectively was: ~7.5 µm and ~30 µm, the height of pillars: ~20 µm and ~60 µm, the diameter of pillars ~3 µm and ~12 µm. Pillars fabricated by the single laser exposure were strong in the center of the exposed area and they were standing straight, while on the edge of the exposed area the pillars were weak and they collapsed (Fig. 4(a)). The reason was the Gaussian spatial beam profile of the laser beam with higher intensity in the center.

Fig. 4. (a) Pillar array with a period of 7.5 µm fabricated by a single laser exposure (1 s, 20 000 pulses) using four-beam interference in SZ2080 with 1 % concentration of 4,4’-bis(dimethylamino)benzophenone; (b) enlarged view of pillars array with a period of ~7.5 µm fabricated by single laser exposure; (c) pillars array with a period of ~30 µm fabricated with an average power ~1.5 W and repetition rate ~ 5 kHz by a single laser exposure (5 min, 1.5×10⁶ pulses) using four-beam interference in SZ2080 with 2 % concentration of 4,4’-bis(dimethylamino)benzophenone.

As was mentioned before the processed area depended on the initial beam diameter and focal lengths of used lenses in experimental setup. In order to fabricate periodic structure over the area larger than the beam overlapping area, more than a single laser exposure should be applied. Each laser exposure should be shifted by a fixed period to each other. By choosing a proper hatch (fixed period) and scanning direction between laser exposures, periodic micro-structures can be expanded over a large area. The example of the fabricated periodic micro-structure over a
large area by using four-beam interference and more than one exposure is shown in Fig. 5 (a). These fabricated periodic micro-structures can be used as artificial scaffolds in tissue engineering and regenerative medicine.

In this paper we demonstrate fabricated pillar arrays with periods of 7.5 μm and 30 μm and micro-lenses array over a large area in SZ2080 by the multi-photon polymerization technique via four-beam interference. By using this technique, it was possible to fabricate periodic micro-structures with different period. The theoretical limit of the smallest period follows from diffraction limit and is equal to a half of the used laser wavelength ($\lambda_{\text{voltage}}/2$). Limitation of the practical smallest and largest periods of micro-structures follows from limits of the used experimental setup (laser power, clear aperture of used lenses, etc). By choosing a proper hatch (fixed period) and translation direction between laser exposures, periodic micro-structures can be expanded over a large area (up to mm), therefore the used interference technique is a very promising technique for mass production of periodic structures for variety of practical applications, such as production of micro-optical/photonic components and artificial scaffolds due to time-saving and simplicity of the features.

4. Conclusions

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