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Fabrication of Periodic Micro-Structures by Multi-Photon Polymerization Using the Femtosecond Laser and Four-Beam Interference

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Multi-photon polymerization by interference is a promising technique for mass fabrication of 3D periodic micro-structures over large areas, which can be used in various fields such as biomedicine (cell growing), photonics (photonics crystals), etc. As direct laser writing approach is a relatively slow process, fabrication of periodic structures by interference field of a few laser beams can be a significantly faster alternative route of parallel processing. The periodic structures are produced by the single laser exposure over the whole irradiated area. In this paper we present examples how periodic micro-structures can be fabricated over a large area by multi-photon polymerization in a negative photopolymer SZ2080 (ORMOSIL) using four-beam interference of a femtosecond laser.

Keywords: Multi-photon polymerization, periodic micro-structures, interference, SZ2080, ORMOSIL, femtosecond laser.

1. INTRODUCTION

Direct laser writing based on multi-photon polymerization (MPP) is a powerful technology to generate three-dimensional (3D) micro-structures with high resolution, but fabrication by this technique is time consuming and hardly acceptable for industrial batch production even when the sample size is only (100×100) microns large [1]. Solution of the problem can be in use of the laser beam interference. Fabrication of periodic micro-structures by multi-beam interference in a large area is much faster than fabrication by the direct laser 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.

2. BASICS OF MULTI-PHOTON POLYMERIZATION (MPP) AND FOUR-BEAM INTERFERENCE

MPP is based on absorption of two or more photons simultaneously. The coefficient of two-photon absorption (2PA) is proportional to the square of the light intensity. Thus to observe this kind of non-linear absorption, a laser with a high intensity of radiation is needed. As mentioned above, in a MPP process, two or more photons are absorbed simultaneously by a photo-initiators molecule. Since the cross-section for 2PA is by some orders of magnitude lower than for single photon absorption, the excitation beam intensity should be in the range of TW/cm^2 [2] to generate sufficiently high density of the radicalized molecules, especially when using photo-initiators that are not optimized with respect to high 2PA cross-section [3].

Photo-polymers, which are used in fabrication process by multi-photon polymerization, generally consist of two parts: monomers and photo-initiators. Most monomers do not produce an initiating species for polymerization, so it is necessary to introduce low-molecular-weight organic compounds that act as photo-initiators. A photo-initiator due to absorption of suitable photon energy is transformed into reaction-initiating species such as radicals. An ideal photo-initiator should be easily synthesized, low priced, non-toxic, odorless, highly shelf-stable, and have a high absorption of incident light and a high quantum yield [4, 5]. Eqs. (1)–(3) show a scheme of the energy transfer between the photo-initiator and the monomer [4]:

$$I \xrightarrow{h\nu} I^* \rightarrow R\bullet, \tag{1}$$

$$R\bullet + M \rightarrow R-M\bullet \xrightarrow{M} R-M-M\bullet \xrightarrow{M} R(M)_n\bullet, \tag{2}$$

$$R(M)_n\bullet + R(M)_m\bullet \rightarrow R(M)_n + R(M)_m. \tag{3}$$

Here I, I^*, $R\bullet$, M, $M\bullet$ denote a photo-initiator, an intermediate state of I after absorbing a photon, a radical, a monomer, a radicalized monomer, respectively; $h\nu$ refers to energy of the absorbed photon; n and m are the numbers of monomer units. Once the photo-initiator absorbs a photon (1), it is raised to an electronically excited state (I^*); its lifetime is generally very short, often of the order of 10^{-6} s [6]. The excited photo-initiators may be involved into three processes: (i) decay back to the initial state of the photo-initiator with emission of light or heat; (ii) quenching of the monomer in contact with oxygen or by quenching agents; (iii) chemical reaction yielding the initiator species such as a radical. The rate of the yielding initiation for polymerization (R_i) is expressed as follows [4, 6]:

$$R_i = I_{abs} \times F \times f, \tag{4}$$

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where the symbols represent the intensity of light absorbed by photo-initiators (I_{abs}), the fraction of the excited photo-initiator after absorbing light (F), and the fraction of the initiator which initiates polymerization (f). Generally, it is desirable that the rate of initiation should be high and uniform for an effective polymerization. In Eq. (2) a radical formed by the photo-initiator reacts with the monomer to produce the monomer radical (RM), which combines with new monomers, and elongates the polymeric chain (chain propagation). The radical polymerization process is terminated when two monomer radicals meet each other, as described in Eq. (3) [4]. The last step of fabrication process is the development process. The post-exposure development process is used for separation of polymerized and non-polymerized volume of the photopolymer and dissolves the not exposed volume for the negative photopolymer. In case of positive photopolymers, the exposed volume will be dissolved. By scanning the tightly focused laser beam inside the photopolymer volume, in principle, any arbitrary three-dimensional connected structure consisting of voxels can be written directly into the photopolymer [1]. A simplified process of the micro-structure fabrication based on multi-photon polymerization is shown in Fig. 1.

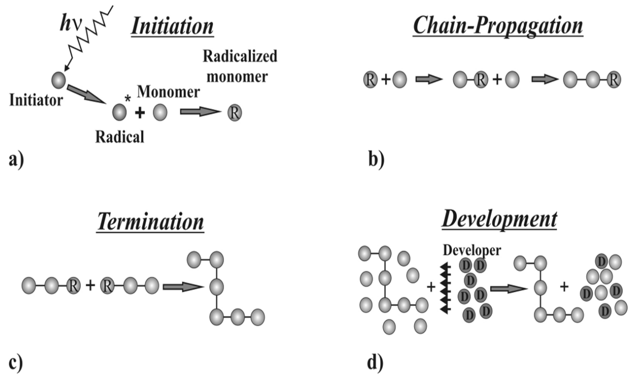


Fig. 1. Process of micro-structure fabrication based on multi-photon polymerization: a – initiation of polymerization reaction; b – chain-prolongation of polymerization reaction; c – termination of polymerization reaction; d – development of fabricated structure

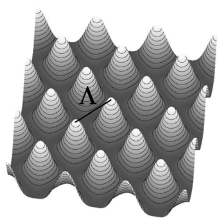


Fig. 2. Intensity distribution in case of four-beam interference when phase shift between beams $\Delta\varphi = 0$; Λ is the period of four-beam interference pattern

The time required for fabrication of structures by the laser direct write technique can be long due to serial process flow from voxel to voxel. Parallelization of the fabrication process can be achieved using multiple laser beams [7, 8]. Interference of four laser beams transforms the intensity distribution of the radiation to periodically distributed maxima as shown in Fig. 2 and they can be applied as the method for rapid fabrication of periodical structures by the simultaneously exposure of the photoresist over the whole area covered by the unfocused laser beam.

3. EXPERIMENTAL SETUP

Experimentally polymerization using the four-beam interference was realized using an experimental setup shown in Fig. 3.

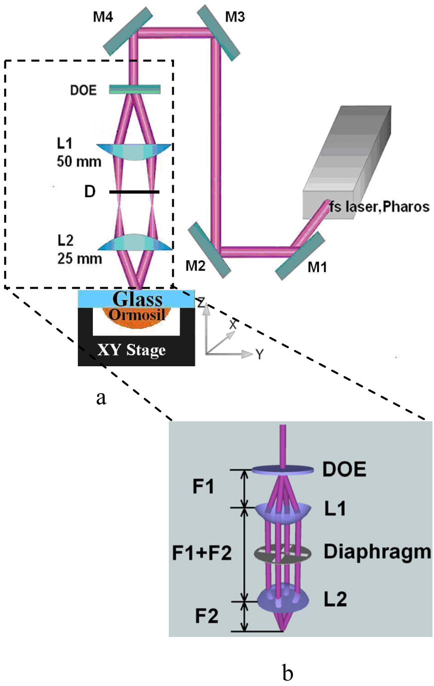
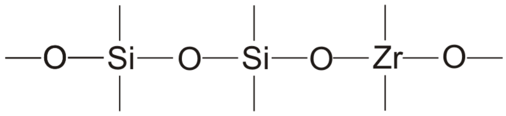


Fig. 3. Experimental setup of multi-photon polymerization by four-beam interference – (a); enlarged fragment of laser setup (4F imaging system) – (b)

Experimental setup included: a femtosecond laser Pharos-6W (1030 nm, ~290 fs, 200 kHz, Light Conversion Ltd.), a diffractive optical element (DOE, MS0202, HoloOr Ltd.), two lenses (L1 and L2) with focal lengths of 50 mm and 25 mm, positioning system XYZ, diaphragm (D) and a few 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 identical beams. The diaphragm was used to block undesirable beams that appear after splitting the laser beam with 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 (Ormosil) [9] (FORTH, Greece) with 1 % concentration of photoinitiator 4,4‘-bis(dimethylamino)benzophenone.

Chemical formulas of SZ2080 and 4,4‘-bis(dimethylamino)benzophenone and absorption spectrum of SZ2080 are shown in Fig. 4.

Our goal was to fabricate periodic micro-structures over a large area by four-beam interference in a negative photopolymer SZ2080. Using four-beam interference based on multi-photon polymerization technique we fabricated a pillar array with the period of ~7.5 µm. This period between pillars depends on the focal length of lenses in the experimental system. By changing the focal length of lenses it was possible to fabricate a pillars array



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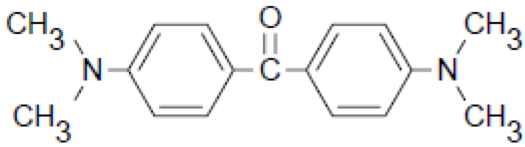

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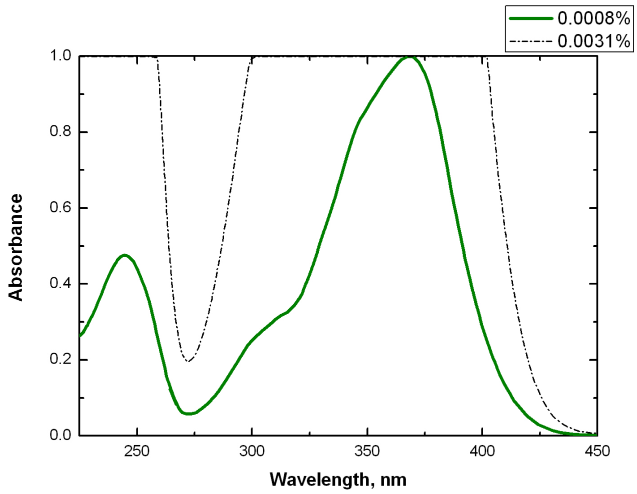


c

Fig. 4. Chemical formula of SZ2080 (Ormosil) – (a); chemical formula of 4,4‘-bis(dimethylamino)benzophenone – (b); absorption spectrum of 4,4‘-bis(dimethylamino)benzophenone (0.0008 % in methanol) [10] – (c)

with different periods. Relation between the period of four-beam interference pattern and focal length of lenses can be expressed as:

$$\Lambda = \frac{d}{2} \frac{F_2}{F_1}, \quad (5)$$

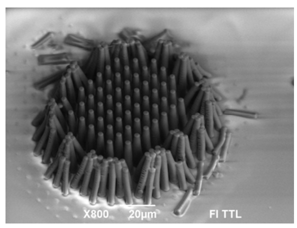
where Λ is the period of four-beam interference pattern (shown in Fig. 2), d is the grating period of DOE, F_1 is the focal length of the first lens in 4F system, F_2 is the focal length of the second lens in 4F system.

The grating period of the used DOE was 30 µm. The focal length F_1 of the first lens L1 was 50 mm, the focal length F_2 of the second lens L2 was 25 mm. The period of four-beam interference pattern Λ estimated from (5) was 7.5 µm. The theoretical value of the period of interference pattern which was calculated by (5) matches the practically obtained pillar period (Fig. 5).

4. RESULTS AND DISCUSSION

Structures fabricated by a single laser exposure are shown in Fig. 5. Laser parameters were: average power ~0.4 W, repetition rate – 20 kHz, exposure time – 1 s (20000 pulses) for Fig. 5, a, and Fig. 5, c; exposure time for Fig. 5, b, was 0.1 s. The period of fabricated structures in Fig. 5, a, and Fig. 5, c, was ~7.5 µm, the height of pillars was ~20 µm, the diameter of pillars – ~3 µm. Pillars fabricated by the single laser exposure are strong in the center of the exposed area and they are standing straight, while on the edge of the exposed area the pillars are weak and they collapse (Fig. 5, a). The reason of it is the Gaussian spatial beam profile of the laser beam with higher intensity in the center. When the laser exposure time was too short, the structure was weak and collapsed by the development process due to capillary forces (Fig. 5, b). Capillary forces exerted during development and rinse can easily deform and even disintegrate the recorded pattern, especially when feature sizes are small [11 – 13].

When fabricated structures were too high (>25 µm), they also collapsed. The highest aspect-ratio of fabricated pillars which were standing straight and did not collapse was ~ 8 (height ~25 µm, width ~3 µm). Pillars with a higher aspect ratio collapsed. Fabricated high structures are shown in Fig. 6. The height of these structures was from ~100 µm (Fig. 6, a, and Fig. 6, c) to ~150 µm (Fig. 6, b). Because interference field acts in the whole thickness of the photopolymer layer (Fig. 6), the height of our fabricated structures depends only on the used photopolymer layer thickness.



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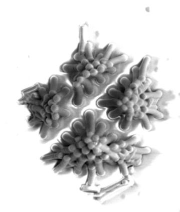

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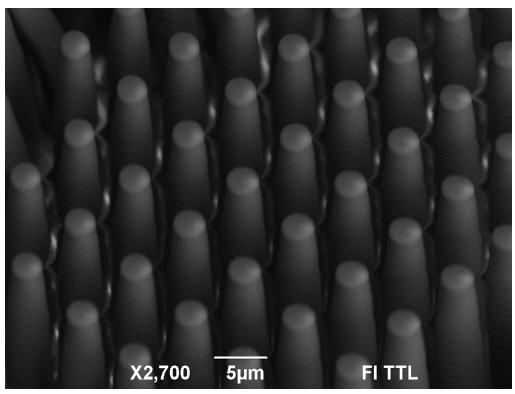

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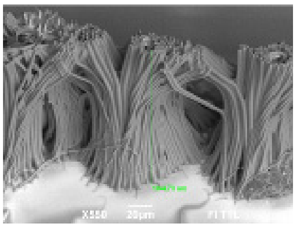
Fig. 5. Pillar array fabricated by a single laser exposure using four-beam interference in SZ2080 with 1 % concentration of 4,4‘-bis(dimethylamino)benzophenone: a – exposure time – 1 s (20000 pulses); b – exposure time – 0.1 s (2000 pulses); c – enlarged view of pillar array fabricated by single laser exposure (exposure time – 1 s (20000 pulses)

All structures were fabricated by the standard developing process (using developer 4-methyl-2-pentanone (isobutylmethyl ketone)). In order to fabricate structures with a very high aspect-ratio (more than 8) different drying process of structures should be chosen. Distortions of patterns can be avoided altogether by applying supercritical drying (SCD) in wet processing [11, 14, 15].



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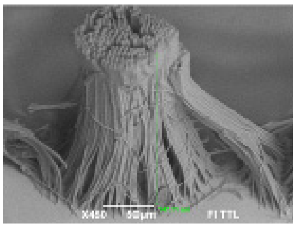

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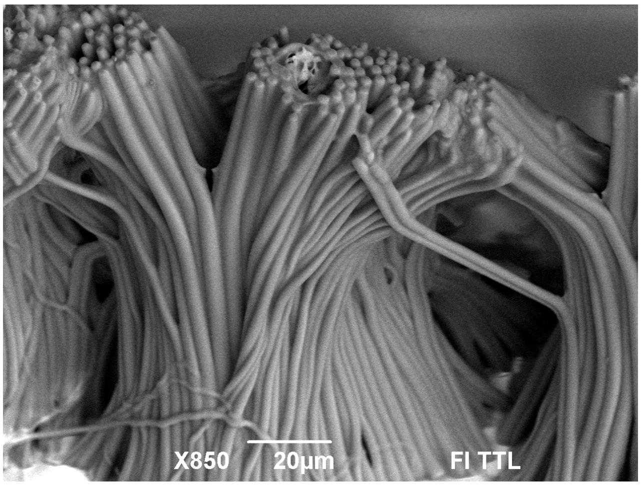
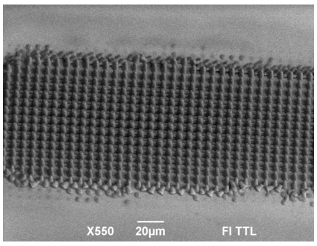
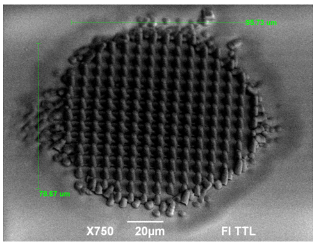


c

Fig. 6. High structures fabricated in SZ2080 by four-beam interference based on MPP technique. Height of structures: a – ~100 µm; b – ~150 µm; c – ~100 µm



a



b

Fig. 7. Periodic structure fabricated over a large area by shifting the single laser exposure – (a); the periodic structure fabricated by the single laser exposure – (b)

The periodic micro-structure fabricated over a large area is shown in Fig. 7, a. The micro-structure was fabricated by shifting the single laser exposure (Fig. 7, b) a few times by 30 µm. Laser parameters during fabrication were: the average power ~0.82 W, the repetition rate – 20 kHz, the exposure time – 0.5 s (10000 pulse), the laser spot size ~80 µm. The chosen shifting step was equal to four periods of the fabricated micro-structure. It is very important to choose a proper shifting step and direction of scanning during fabrication of periodic micro-structures, otherwise the fabricated structure will be non-periodic.

As the laser exposure time for fabrication of the periodic structure in Fig. 7, a, was very short (0.5 s) and the laser spot size was relatively large (~80 µm), it was possible to fabricate periodic structures over a large area very fast by using the interference technique compared with the direct laser writing technique. Thus, the interference technique is very promising for mass fabrication of periodic structures.

The experimental results provided here are the initial step of combining the multi-photon polymerization technique via four-beam interference exposure and novel ultra-low shrinking material SZ2080. Though the fabrication method is not unique by itself [16, 17], but non-linear lithography approach enables easier fabrication of 3D structures as well as higher spatial resolution [3, 11] and the used material is known to have unmatched micro/nano-structuring properties for applications in photonics, microoptical components and extracellular matrixes [18 – 20]. Thus, continuation of this activity will expand the fabrication possibilities from the "proof of principal" stage to the level of the functional device production for practical applications.

5. CONCLUSIONS

We have fabricated periodic micro-structures over a large area in SZ2080 by the multi-photon polymerization technique using four-beam interference. In fabrication of periodic structures by the mentioned technique there are two very important things: 1) to choose a proper hatch and scanning direction between laser exposures; 2) to choose the right laser pulse energy. The used interference technique is a very promising technique for mass fabrication of periodic structures for biomedicine and photonics applications due to time-saving and simplicity features.

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