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Nanostructures fabricated by laser interference lithography and their potential applications

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Abstract

We introduce a rapid and flexible method for polymeric nanostructure fabrication by using four-beam interference lithography. The influence of the laser processing parameters (peak pulse intensity, the number of laser beams, etc.) and photopolymer thickness to the shape of these nanostructures are analyzed, and the shape formation of nanostructures is explained. Also, the potential applications of the structures fabricated by interference lithography are discussed.

Keywords: Nanostructures, multi-photon polymerization; interference lithography, photonics, micro-optics, scaffolds.

Nanostructures have drawn much attention in the past ten years due to their potential applications in biomedicine [1], photonics [2] and plasmonics [3]. They can be fabricated by using various techniques (direct laser writing, electron-beam lithography, soft lithography, etc.). The higher nanostructures fabrication process efficiency can be achieved by the parallel processing technique using the interference of several laser beams [4-7]. Depends on the interfering beams parameters (phase, the angle between beams, number of beams, used wavelengths, etc.) [6] different types of nanostructures are possible to form.

The fabrication technique based on the interference lithography (IL) [4, 5, 8] is among the most practical and elegant approaches to the fabrication of extended periodic micro- and nanostructures [9]. IL is based on the multi-beam interference phenomenon. Interference of electromagnetic waves takes place when at least two coherent beams, propagating at a certain angle to each other, interact. The interference intensity profile in the overlapping area can be in a general case expressed by equation [10]:

$$I(\vec{\mathbf{r}}) \propto \left\langle \left(\sum_{i=1}^{N} \vec{\mathbf{E}}_i (\vec{\mathbf{r}}, t) \right)^2 \right\rangle, \qquad (1)$$

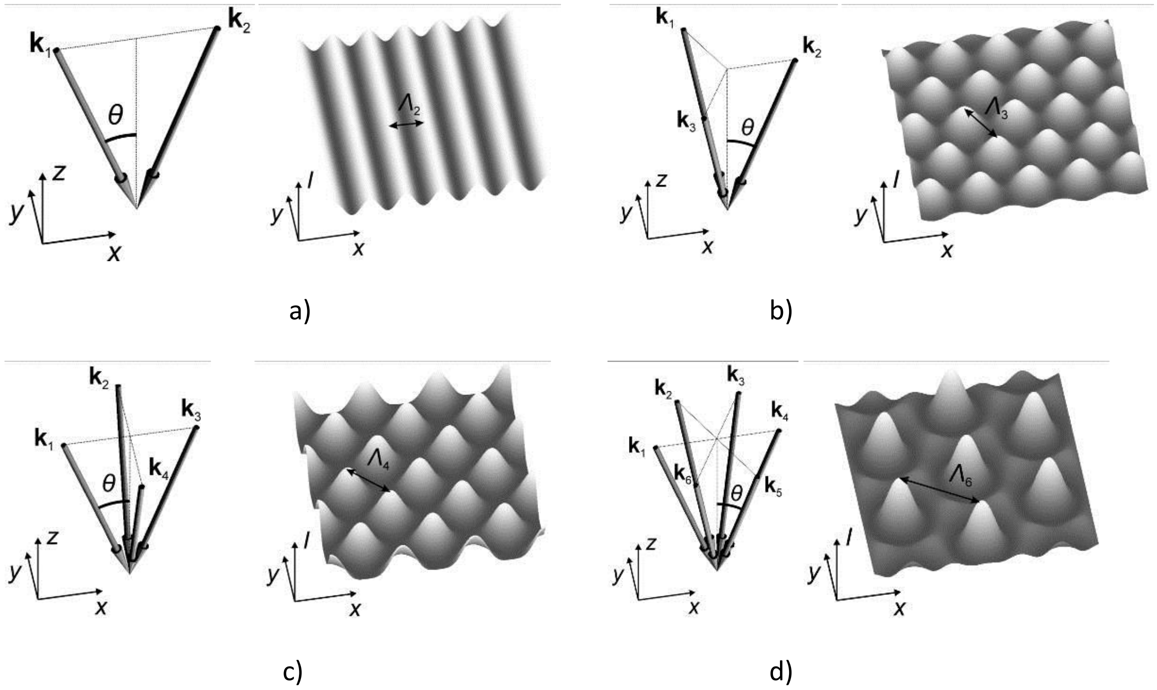
where $\vec{E}_i$ is the electrical field of the i-th beam; $\vec{r}$ is the coordinate vector; i is the index of interfering beams; N is the number of the beams; t is time. Brackets denote averaging over time at least for one period of electromagnetic field oscillations. The electrical field of the i-th wave can be expressed as follows:

$$\vec{\mathbf{E}}_i = \vec{\mathbf{E}}_{0i}\cos\left(\vec{\mathbf{k}}_i \cdot \vec{\mathbf{r}} - \omega t + \varphi_i\right) \tag{2}$$

where $\left|\vec{\mathbf{E}}_{0i}\right|$ is the electrical field amplitude of the i wave, $\left|\vec{\mathbf{k}}_i\right| = 2\pi/\lambda$ is the wave vector of the i-th wave; λ is the wavelength of radiation; ω is the frequency of radiation; ϕ_i is the phase of the i-th wave. When frequencies of all laser beams are the same, Eqs. (1) and (2) can be simplified as follows [11]:

$$I(\mathbf{r}) \propto \frac{1}{2}\sum_{i=1}^{N}\left|\vec{\mathbf{E}}_{0i}\right|^2 + \sum_{j<i}^{N}\sum_{i=1}^{N}\vec{\mathbf{E}}_{0i}\cdot\vec{\mathbf{E}}_{0j}\cos\left(\vec{\mathbf{k}}_i\cdot\vec{\mathbf{r}} - \vec{\mathbf{k}}_j\cdot\vec{\mathbf{r}} + \varphi_i - \varphi_j\right) \tag{3}$$

The period of the formed periodical intensity field depends on the incident angle between the beams and the wavelength of laser radiation. The shape of the pattern depends on the number of beams and the phase difference between them. The periodical intensity distribution patterns of several setups of symmetrically arranged beams are calculated by using Eq. (3) and are presented in Fig. 1.



a) b) c) d)

Fig. 1. Wave vectors of the interfering beams and intensity distribution in the interference field of symmetrically arranged laser beam calculated by using Eq. (3): a) two; b) three; c) four; d) six-beams. XYZ denotes a coordinate system, I is the intensity distribution of the interference pattern, k1, k2, k3, k4, k5 and k6 are the wave vectors of the interfering beams, θ is the angle between the beam and z direction.

The shape of structures fabricated by IL depends on the intensity distribution of the interference field. It is possible to fabricate 1D, 2D and 3D periodic structures by a single laser exposure by recording the multi-beam interference pattern into photoresist. Depending on the laser wavelength, the exposure can be achieved via linear [12] or nonlinear absorption [13]. IL allows fabricating periodic structures over a large area relatively fast and that makes this technique attractive and promising for mass-fabrication of the functional devices such as photonic crystals [14-17] or scaffolds [18, 19]. IL has certain advantages over the direct laser writing (DLW) technique [20] due to the rapid fabrication of periodic structures. The photo-polymerization process is induced in the focal region of a tightly focused laser beam. Any 3D shapes can be recorded in the photosensitive material by translating of the focal spot. The laser wavelength must be selected in the transmission window of the polymer. Therefore, two- or even three-photon processes are involved. For this reason, high laser intensities are required. Therefore, femtosecond lasers are usually used for multi-photon laser polymerization. Only one voxel (volumetric pixel) is fabricated by a single laser exposure in the focal area of the objective using the DLW technique. In the IL technique, a periodic structure is formed in the whole area irradiated with the overlapping laser beams using a single laser exposure. IL technique is a fast mean of periodic structure fabrication. However, not every desired shape of the structure can be fabricated by IL as in the case of DLW. IL technique enables fabricating only periodic structures which correspond to the beam interference pattern.

In this article, we present the ability of the IL technique to fabricate microstructures suitable for microfluidics, micro-optics, and tissue engineering. All microstructures were fabricated by using the same experimental setup consisting of a femtosecond Yb:KGW laser (Pharos, Light Conversion) generating ~ 250 fs pulses at 1030 nm or 515 nm (second harmonic), a diffractive optical element (DOE) (Holo-Or Ltd.) which split the laser beam into four identical beams, diaphragm which blocks undesirable high-order diffracted beams and a two-lens imaging system that collects the four-beam in the sample where they interfere. The interference intensity distribution of four-beam in the vertical direction is constant and fluctuates only in the horizontal direction (depicted in Fig. 2).

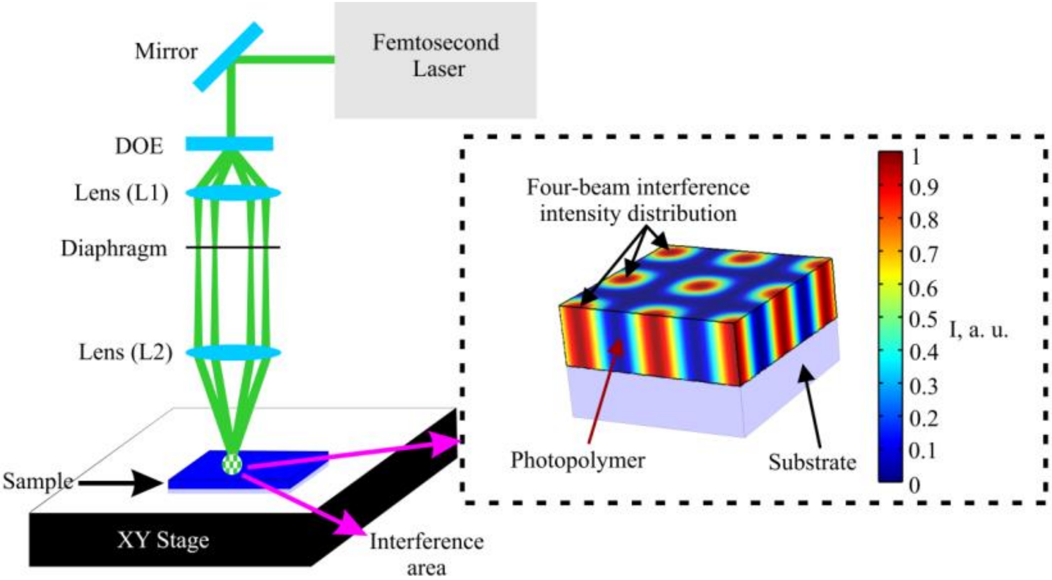
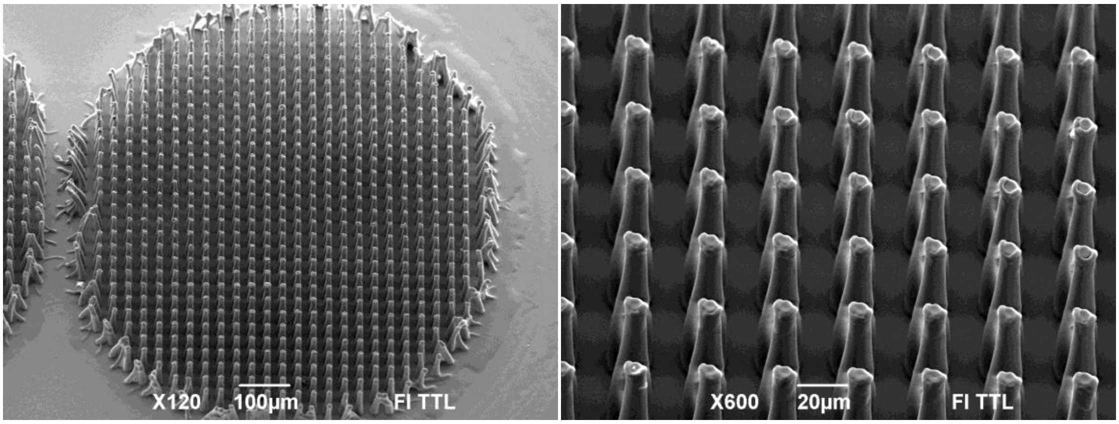


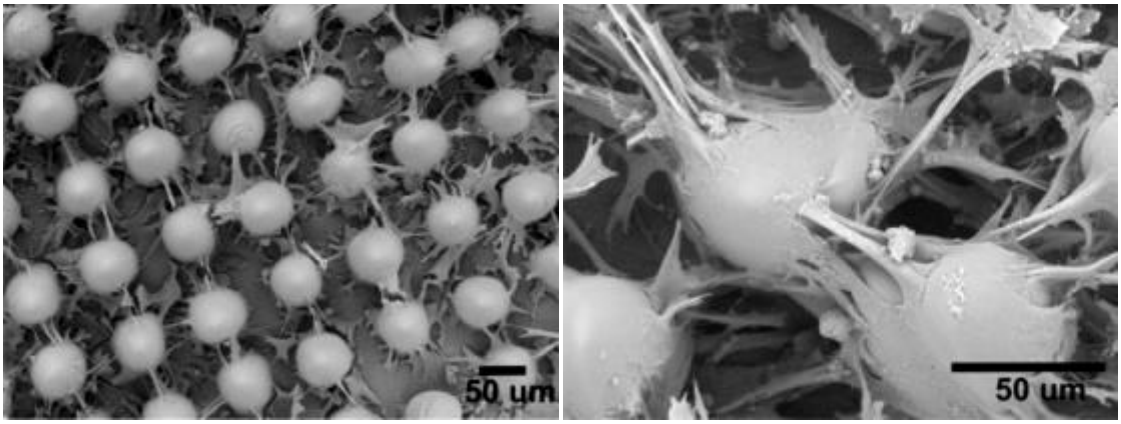
Fig. 2. Typical experimental setup of four-beam interference lithography.

Typical microstructures fabricated by using four-beam interference lithography are micro-pillar array (Fig. 3). By changing the laser processing parameters (wavelength, average laser power, exposure time, beam polarization, phase etc.) the shape of fabricated microstructures can be controlled [6]. Structures similar to shown in Fig. 3 can be applied in tissue engineering for investigation of cell behavior (proliferation, migration, adhesion, etc.). IL is a very suitable technique to fabricate such structures for tissue engineering as the method is not time consuming technique and a whole array of micropillars can be fabricated by a single exposure in the large area (> 1 mm). The example of the use of the periodical structures fabricated by IL technique for tissue engineering is shown in Fig. 4.



a) b)

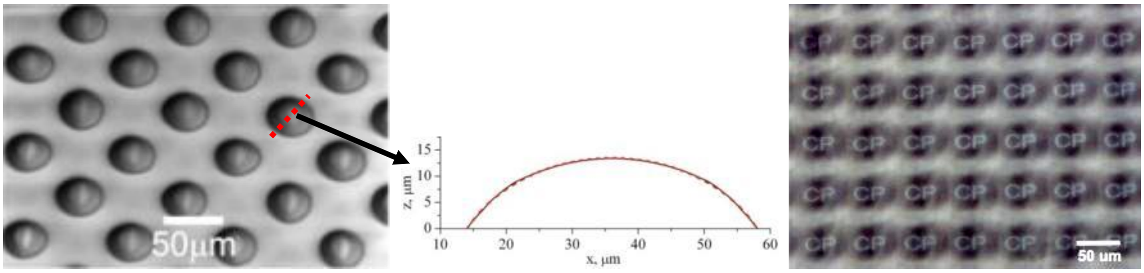
Fig. 3. a) Pillar array with a period of 30 μm fabricated by a single laser exposure (5 min, 1.5×10^6 pulses) using four-beam interference in SZ2080 with 2 % concentration of 4,4′-bis(dimethylamino)benzophenone and 1030 nm laser wavelength; b) Enlarged view of pillars array depicted in a). SEM images of the structures are tilted by 34 deg.



a) b)

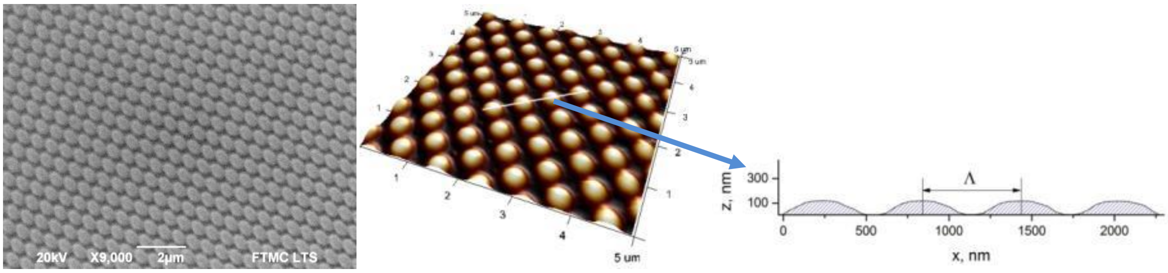
Fig. 4. SEM images of structures with a period of 90 μm fabricated from PEG-DA-258 with rabbit myogenic stem cells grown for four days (different magnifications shown).

Recently, we have demonstrated the ability to fabricate microlens array using IL [21]. SEM micrographs of microlens array structures fabricated using four-beam interference lithography are shown in Fig. 5a. The curvature radius of fabricated microlenses is ~ 25 μm (Fig. 5b). It is possible to control the geometrical parameters of the fabricated microlenses by managing the laser irradiation dose [21]. The optical performance of fabricated microlenses is shown in Fig. 5c. The letters “CP” are clearly imaged by the fabricated microlenses. By decreasing the period of fabricated structures, it is possible to form diffractive optical element for IR and visible range. The decreasing of the period can be achieved by increasing the angle between interfering beams or decreasing the wavelength of used laser irradiation. The smallest period, which was achieved using second harmonic (515 nm) of “Pharos” femtosecond laser was ~ 600 nm. The example of such fabricated microstructures is shown in Fig. 6.



a) b) c)

Fig. 5. a) Microlenses fabricated by four-beam interference lithography using the laser average power of 630 mW (~ 0.7 GW/cm^2 peak pulse intensity) and laser exposure time 10 s. The period between microlenses is ~ 60 µm. Laser processing parameters were: wavelength – 515 nm, repetition rate – 100 kHz. SEM images of the structures are tilted by 34 deg; b) The profile of microlens dashed in a); c)„CP“ letters imaged by microlens array shown in a).



a) b) c)

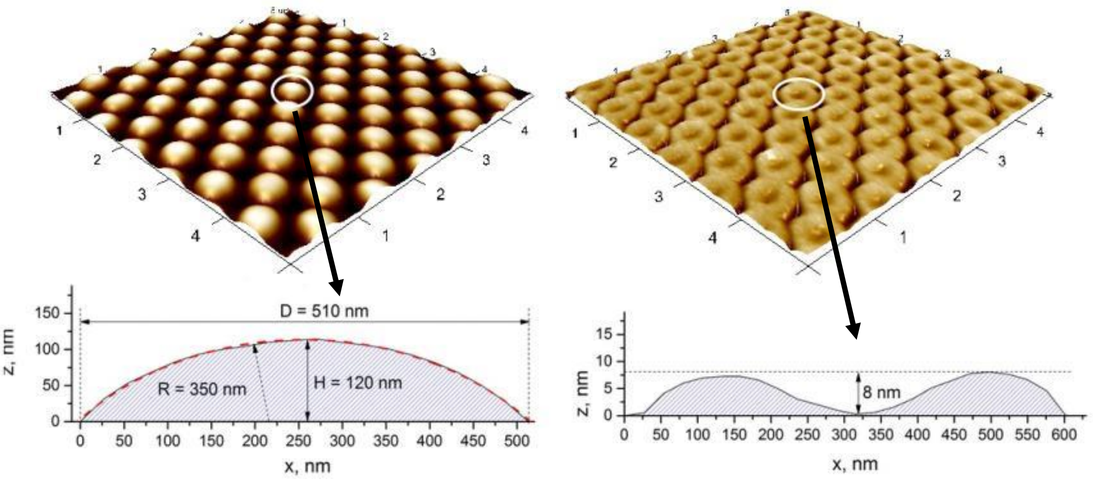
Fig. 6. Nanostructures array with 600 nm period fabricated by four-beam interference lithography: a) SEM micrograph; b) AFM image tilted by 45 deg; c) The profiles of nanostructures marked in b) (Λ=600 nm).

By fabricating structures with a small period (less than 1 µm), the diffusion rate of monomers and the photo-polymerization reaction rate competes with each other during the formation process. The most desirable conditions for fabrication of the hemispherical shape structures exist when the diffusion rate is a few times larger than the reaction rate [22]. In this case fabricated nanostructures have the shape of plano-convex lenses (Fig. 7a). By increasing the peak intensity in the interference maximum, the photo-polymerization reaction rate is also increasing, and the shape of fabricated structures due to this process is changing. In this case, the photoreactions take place too fast to transport monomers by diffusion from far away before the monomer is entirely consumed by photoreaction. The result of it is that the fabricated structures have a pit at the center (Fig. 7b). These both structures were fabricated in the same thickness of photopolymer. In Fig. 7b is shown only the top of the profile of microstructures as the bottom of fabricated microstructures start to overlap each other and only in the top is still possible to distinguish details of fabricated structures. As interference field in the vertical direction can reach several millimeters, the thickness control of a photopolymer is also necessary for the fabrication process. The control of photopolymer thickness can be realized by using a spin-coater and by diluting the photopolymer with fast-evaporating liquid (for instance: isopropanol). The example of fabricated structures in the thick photopolymer is shown in Fig. 8. The critical Young’s modulus (E_{kr}) for the pillars to withstand capillary drainage is given by [23]:

$$E_{kr} = \frac{24\gamma H^4}{(2r)^3 \Lambda^2} \qquad (4)$$

where r is the radius of the pillar; H is the high of the pillar; γ is the surface tension coefficient; $\Lambda = x - 2r$ is the period between the pillars.

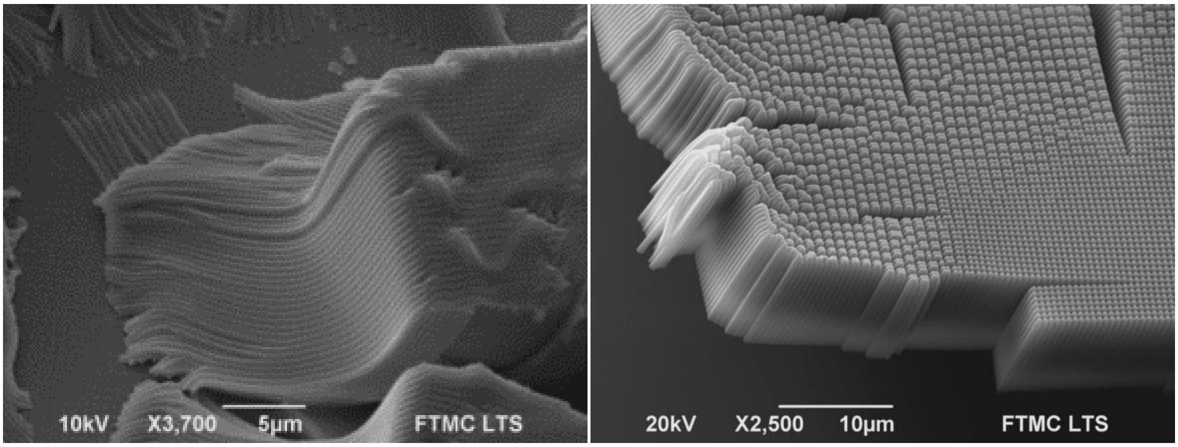
As can see from Eq. (4), the critical Young's modulus is higher for a smaller period of thinner and higher pillars array. It means that the thinner and higher pillars array with the smaller period, the harder to fabricate the free-standing pillar arrays.



a)

b)

Fig. 7. AFM profiles of periodic microstructures arrays with 600 nm period fabricated using different laser pulse peak intensities: a) 0.91 GW/cm^2 and b) 18.1 GW/cm^2.

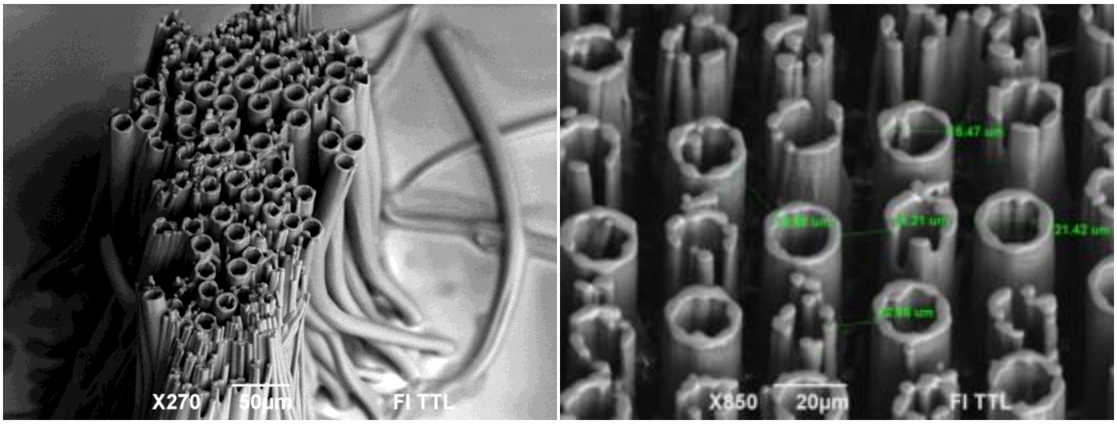


a)

b)

Fig. 8. The high pillar arrays fabricated by IL in different thickness of photopolymer SZ2080: a) ~ 30 μm and b) ~ 18 μm.

Moreover, we have already demonstrated that more complex structures such as microtube arrays [24] suitable for microfluidics applications can be fabricated by using IL technique. These structures were fabricated by rotating the sample during the IL processing (Fig. 9).



a) b)

Fig. 9. The microtube array fabricated using the IL method (different magnifications shown). Process parameters: the average laser power ~ 300 mW; the repetition rate 5 kHz, the exposure time ~ 1 min.

Conclusions

Fabrication of various periodic structures by using interference lithography is demonstrated. The shape of the fabricated microstructures depends on many factors of the interfering beams such as the polarization, the number of the interfering beams, the phase shift, the laser irradiation dose, the angle between interfering beams, the wavelength, etc. By fabricating structures with a small period (less than 1 μm), the diffusion rate of monomers and the photo-polymerization reaction rate competes with each other during the formation process. This competition determines the shape of fabricated nanostructures. When the photoreaction rate was larger than the diffusion rate, the photoreactions took place too fast to transport monomer by diffusion from far before monomers were entirely consumed by the photo-reaction. The result of it is that the fabricated periodic structure has a pit at the center of the structure. For fabrication of nanostructures with the a shape of the plano-convex lens, it is required that the diffusion rate of monomers must be much larger than the photoreactions rate. The fabricated periodic structures using IL have the potential to be used for various applications such as photonics - for light localization, micro-optics – for light guiding, biomedical - for the investigation of stem cell behavior, microfluidic – for controlling the flow of fluids on small length scale or in tissue engineering by creating an artificial vessels.

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