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High-aspect-ratio structures produced by two-photon photopolimerization

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In this work microstructures with high-aspect-ratio were produced by two-photon photopolymerization technique in SU-8 photoresist. When micrometer or submicrometer size features are realized, the standard protocol for processing the photoresist has to be adapted to the dimension of the desired structures. Using the suitable parameters of the protocol for exposure and development of the photopolymer, microstructures with aspect-ration more than 10:1 were obtained.

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1. Introduction

The nonlinear effect of two-photon photopolymerization (TPP) in photoresists was intensively used in the last years for developing the micro-stereo-lithography technique [1-5]. 3D microstructures can be realized by NIR femtosecond lasers processing in materials which are normally transparent to the NIR radiation. When a femtosecond laser beam is focalized in the volume of a transparent photoresist, due to the high peak intensity in the focused spot, a high probability of two-photon [6] or multiphoton absorption occurs [7].

A large series of photoresists such as SU-8, Ormocers, KMPR, PMMA, etc. has the maximum of the absorption band in the UV-blue spectral range. In such photopolymers the two-photon absorption of NIR femtosecond laser pulses induces photochemical reactions and then photopolymerisation, just like in the case of single UV photon absorption. In contrast with the single photon processing, the two-photon absorption occurs in a very tiny volume of material, at the center of the focused spot, were the laser intensity exceed the photopolymerization threshold. If the lasers fluence is kept just above the TPP threshold, small features can be created with resolution down to tens of nm's [8-9]. Following the rapid prototyping algorithms practically any 3D computer designed geometries can be fabricated. However, in applications such as micro/nanophotonics or microfluidics, some designs are difficult to be realized because of the limited aspect-ratio of the structures, shrinkage and deformation of the polymerized structure.

High-aspect ration up to 40:1 were previously obtained in SU-8 by UV processing of ultra-thick photoresist film [10]. Other techniques such as proton beam writing [11,12], or electron beam writing can be also employed [13]. Ultra-high aspect-ratio on SU-8 up to 100:1 has demonstrated by deep x-ray lithography [14]. However, TPP technique remains the most adapted for realization of fully 3D microstructures. In order to compensate for different geometrical effects, mechanical supports for sustaining the photopolymerized structures have to be produced with a compromise on the total processing time [15,16].

In this paper the limiting factors of aspect-ratio are analyzed and a more adapted processing protocol is proposed for TPP. The process parameters are optimized for obtaining structures with high-aspect-ration in SU-8. When a structure is formed in columnar configuration, during the development of the sample in a solvent for removing the non-irradiated resin, the pillars can brake or collapse to the substrate. In our experiments, by implementing a suitable protocol, we obtained columnar structures with aspect-ratio of about 10:1. The fabrication of such structures will allow the study of new designs for photonic or micro-fluidic devices.

2. Experimental set-up

The SU-8 structures were produced by TPP in a home-made microprototyping system built in a modular and portable configuration. The main modules are: the focusing optomecanics, the translation stages sample, and the visualization system.

In our experiments a 100X Mitutoyo microscope objective numerical aperture NA=0.5 and 12 mm working distance was used for focusing the femtosecond laser. Compared with the immersion microscope objectives with NA higher than 1, the long working distance microscope objectives allow the focusing of the laser beam deeply in the volume of a transparent material.

The sample is translated by a Nanocube stage (Thorlabs) composed by three piezoelectric stages and three XYZ steppers. The total travel range is 4x4x4 mm with hundreds of nm accuracy. For the sample focusing a visualization system with CCD and a 200 mm tube lens is

used. The resolution of the visualization system is less than 1 μm. The processing microscope can be easily coupled with different femtosecond lasers by a 45° dielectric mirror which reflects the laser beam to the microscope objective and transmits the visible light to the visualization system. In this work a SynergyPro laser system from Femtolasers was used. The laser delivers femtosecond pulses with 15 fs pulse duration and 75 MHz repetition rate at 790 nm wavelength with 100 nm bandwidth.

The entire writing process on photopolymers is driven by software which has control on laser writing parameters such as writing speed/exposure time, laser energy, and structures geometry. A procedure for automatic corrections of the planarity of the sample or other mechanical deviation of the translation stage is also integrated in the software.

3. Optimization of the processing protocol

The processing protocol of SU-8 photoresist supposes few steps recommended by Microchem producer. The parameters of the protocol can be slightly different in function of the viscosity of the photoresist and the thickness of the sample. The main steps are: 1- substrate preparation; 2- *deposition* of the photoresist; 3- *softbake* at up to 95 °C for few tens of minutes in function of the thickness of the photoresist layer, for evaporation of the solvent; 4-laser *exposure*; 5-*post exposure bake* at 95 °C for increasing the cross-linking speed and formation of the photopolymer chains; 6- *development* in a specific solvent for removing the non-polymerised photoresist.

The standard protocol in normally used in the case of photopolymerized structures on large substrate surface, such as in the classical photolithography. When very small structures are created by TPP each protocol step has to be adapted for these in order to obtain high-aspect-ratio structures. Some previous works have been focused on the optimisation of exposure step proposing multipath scanning of the sample [17]. Other works proposed optimisation of the softbake or postbake process with a slightly increase of the baking temperature and the process time [18-19]. We found also a strong influence of the development process on the final geometry of the photopolymerized structure as shown in this work. For the study of the protocol parameters we realised a hexagonal network of vertical pillars as a mimic of a 2D photonic crystal. Bellow is presented the optimised protocol we found for creating high-aspect-ratio structures.

3.1 Substrate preparation

For a good adhesion of the photopolymer on the substrate we used a fused silica samples cleaned in ultrasonic bath with acetone and rinsed in distilled water, followed by a dehydration bake at 200° for about 10 minutes. No adhesion promoter was additionally used.

3.2 Deposition

In the deposition protocol step, the thickness of the photoresist layer can be controlled by spin-coating method in the range of few micrometres to tens of micrometres. A spin-coater from Brewer Science, Model 200, was used with spinning speed from 500 up to 12000 rot/min, in function of the desired thickness. SU-8 2025 with viscosity of 4500 cSt was used. For this viscosity layers with thickness up to 100 μm can be obtained. If thicknesses of few hundreds of micrometers are desired, the deposition of the photoresist can be done by simply dropping a small quantity of SU-8 on the surface of the fused silica. In this case the exposure has to be done in the middle of the droplet in order to avoid the optical aberrations on the laser beam introduced by the curved surface of the droplet.

3.3 Soft bake

To completely remove the solvent from the photoresist, the softbake step is realised in air at 110°C on a hotplate for about 30 minutes up to 1 h in the case of thick SU-8 layers. The temperature was gradually increased from the room temperature to the soft bake temperature with a pre-bake at 65°C for 15 min.

3.4 Exposure

Using the visualization system the laser beam is precisely focused at the interface of the fused silica with the photoresist. When the structures are created on a large substrate area, the aspect-ratio is limited by the deviation of sample surface from an ideal horizontal plane, as shown in the Fig. 1.

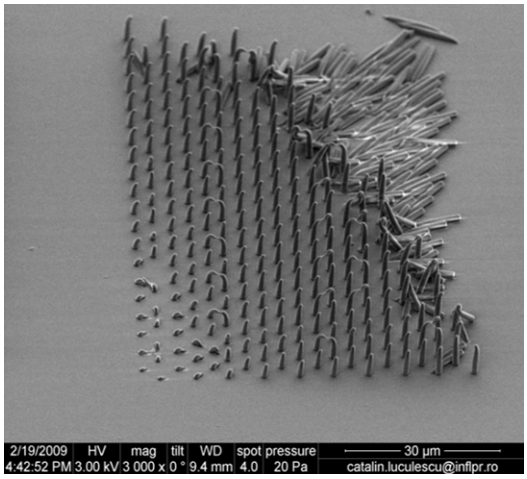

Fig. 1. Effect of the planarity deviation on the aspect-ratio. The pillars disposed in hexagonal symmetry are realized with scanning speed of 10 μm/sec in Z direction at laser power of 20 mW.

Our software for laser processing includes a focusing procedure which allows the correction of the planarity deviation. The sample surface is initially defined by 9 points : $[X_i,Y_j,Z_k]$ around the processing area, with i,j,k = 1 to 3.

These 9 points are determined experimentally from the visualization system. In future development of the system, an autofocusing procedure can be also implemented. For any [X,Y], the correct Z is calculated by interpolation. Then, the mechanical system will automatically correct the Z position when the sample is moved in XY plane. The activation of this option on the software interface will allow the realization of the structure on a large area of the sample following precisely the substrate curvature. Also by this way, any mechanical errors of the translation stage are automatically corrected, such as the cross-talk effect on Z direction or accurate motion.

The columns were realized by translating the sample in Z direction with different scanning speeds from 5 to 100 μm/s, at different laser power from 5 to 60 mW. At higher laser power the creation of bubbles in photoresist was observed. Increasing the exposure-time, higher aspect-ration for 3D structure can be reached. However, this will increase the total processing time. The increase of the exposure-time can be compensated by increasing the laser energy below the damage threshold. However, in this case lower resolution will be obtained. An alternative, as proposed in the Ref. 17, the multipath scanning can be used in order to increase the degree of the polymerisation of the photoresist and the rigidity of the sample.

3.5 Development

After laser irradiation, the non-polymerized resin is removed by developing the sample in PGMEA solvent. During development, when tiny photopolymerized structures were form in columnar configuration, in order to keep the structures vertical, the usual strong agitation of sample has to be avoided. The sample is kept in solvent for few minutes (depending on the thickness of the photoresist), and afterward removed slowly by a mechanical translation stage at a controlled speed.

Even in this case the columns collapsed on the surface.

In order to understand the mechanisms involved in the degradation of the sample during development, the sample is kept under an optical microscope during all the development process. The microscope images of the structures taken during development demonstrate that the columns remains vertical even after complete removal of the non-polymerised resin (Fig. 2a).

The pillars will collapse just at the moment of removing the sample from the solvent (Fig. 2b). This indicates a low rigidity of the structures induce by several factors: insufficient cross-linking of the polymer and/or drenching effects of solvent on the pillars. In order to prevent the gravitational collapsing of them before the drying process, the substrate is kept and removed from the solvent in the up-side-down position. However, the structures are still collapsed after the removal from the solvent, when the experimental configuration is like in the figure 3a. When the sample is slowly and vertically removed from the solvent, because of the strong capillary forces, a high column of liquid solvent remains attached to the substrate.

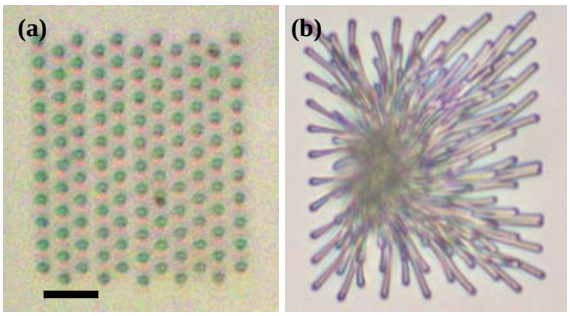

Fig. 2. Top view of the columnar structures: (a) during development process, and (b) the same structure after removing the sample from the solvent. The pillar structure collapses due to the strong capillary forces. Scale bar: 10 μm.

If the height of the solvent column exceed few mm, this will drop very fast inducing a mechanical deformations of the polymerised columns. It seams that the strong capillary forces are responsible for collapsing the columns to the substrate, after development, just at the moment of removing the sample from the solvent.

For minimising the effects of the surface tension, the sample is removed from the solvent after development, at the inclination angle of 20-30° with a controlled speed of 50 micrometers per second (figure 3b). The modified development protocol allows the realization of high-aspect-ration structures by photopolymerization.

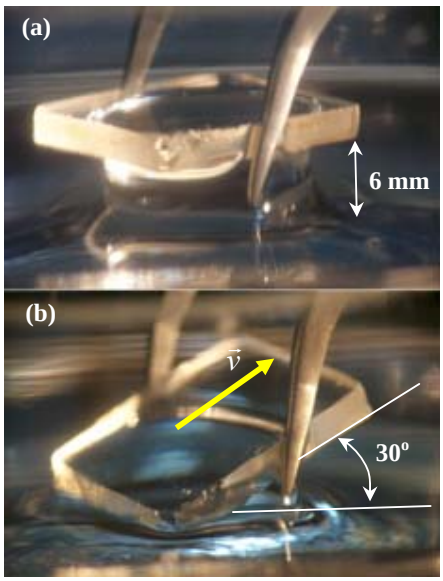

Fig. 3. Development of the photopolymer. In the optimal configuration the sample is removed from the solvent at the inclination angle of 20-30° for preventing the collapse of the high-aspect-ratio structure on the support surface.

4. Results

After the optimisation of the processing protocol, different structures with high-aspect ratio were produced by TPP. In the Fig. 4a is presented the SEM image of a periodic structure realized in SU-8. For visualization, the sample was rotated 45^o for a better observation of the geometries in 3D. The structure consists in vertical columns disposed on the substrate surface in the hexagonal symmetry. In this case the distance between two adjacent columns was 10 μm. The columns were realised by scanning the focused laser beam along the Z direction starting at 1 micrometer below the substrate surface to allow a good adherence of the pillar on the substrate. The exposure parameters were: laser power 60 mW at 50 μm/s laser scanning speed in Z direction. A double path scanning was used in order to increase the rigidity of the pillars.

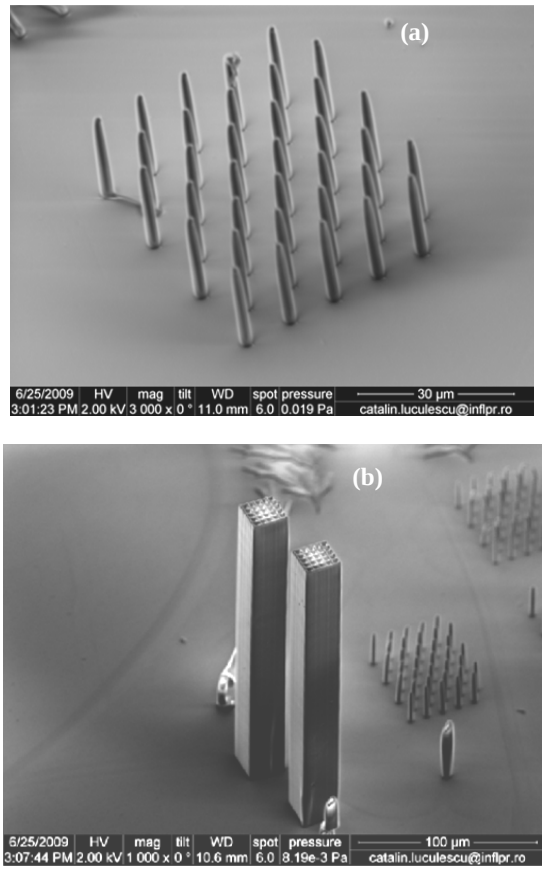

Fig. 4. Structures realized by TPP in SU-8 with aspect-ratio of 10:1. (a) Pillar structures 20 μm high; (b) 3D blocks 200 μm high.

In these exposure conditions the photopolymerized voxel has an ellipsoidal shape with 2 μm in diameter and about 7 μm along the Z axis. From the scanning speed we can estimate the exposure time of about 150 ms per voxel and per single scan. The columns remain vertical when the optimised development was used. From the SEM images we estimated the dimensions of the columns. Their height is 20 μm and the diameter is 2 μm. Then, a 10:1 aspect ratio was produces for pillars structures.

Also, higher structures can be now produced. In the figure 4b is presented the SEM image of vertical blocks as high as 200 μm with 20x20 μm^2 squared base. These structures were built in woodpile geometry with distance between adjacent planes of 2 μm, less that the voxel height, in order to obtain a continuum and smooth vertical wall. The processing parameters were: laser power 40 mW, scanning speed 50 μm/s. In XY direction the diameter of the voxel was 1 μm, and then the exposure time was 20 ms per voxel and per single path. From the dimensions of the blocks we observe an aspect ration of 10:1 with an absolute height of 200 μm.

5. Conclusions

The structures produced with high-aspect-ratio collapse on the substrate due to the strong capillary forces, insufficient laser power and/or exposure time. When the protocol parameters are optimized, columnar structures with aspect-ratio of more than 10:1 can be obtained. The fabrication of high-aspect-ratio structures will allow the study of new microdevices for photonics or microfluidics.

Acknowledgments

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