Lithuanian Journal of Physics, Vol. **50**, No. 2, pp. 201–207 (2010) doi:10.3952/lithjphys.50203

FEMTOSECOND VISIBLE LIGHT INDUCED TWO-PHOTON PHOTOPOLYMERIZATION FOR 3D MICRO/NANOSTRUCTURING IN PHOTORESISTS AND PHOTOPOLYMERS

M. Malinauskas, V. Purlys, M. Rutkauskas, A. Gaidukevičiūtė, and R. Gadonas

Department of Quantum Electronics and Laser Research Centre, Faculty of Physics, Vilnius University, Saulėtekio 10, LT-10223 Vilnius, Lithuania

E-mail: mangirdas.malinauskas@ff.vu.lt

Received 20 October 2009; revised 22 January 2010; accepted 18 March 2010

Laser two-photon polymerization (LTPP) has been widely reported as a tool for three-dimensional micro/nanofabrication. Femtosecond lasers are employed to form nanostructures in photosensitive resins with subwavelength resolution. We demonstrate high throughput large scanning area LTPP system based on linear motor driven stages combined with Yb:KGW high repetition rate (312.5 kHz) amplified laser as irradiation source (515 nm second harmonic's wavelength). Femtosecond green light can be focused to a smaller diffraction limited spot and provides higher structuring resolution comparing to commonly used Ti:sapphire lasers (operating at NIR wavelengths) used for LTPP. Additionally, shorter irradiation wavelength enables to process more of widely used photosensitive materials. The system capacitates production of nanostructures having 200 nm lateral resolution with high repeatability. By modifying focusing optics there is a possibility to scale up the fabrication: reduction of resolution results in shortening of fabrication time. The system enables formation of 3D structures with size varying from tens of microns to tens of millimetres. Most of the materials commonly used for photopolymerization technology (various blends of acrylates, hybrid organic–inorganic materials, and epoxy resins) are well suitable for processing with the constructed LTPP system.

Keywords: two-photon absorption, laser processing, photopolymerization, micro/nanofabrication, three-dimensional structures, tissue engineering

PACS: 42.50.Hz, 82.30.Cf, 89.20.Bb

1. Introduction

Laser two-photon polymerization (LTPP) is a powerful tool for sculpting three-dimensional (3D) microstructures with a nanoscale resolution. This femtosecond laser processing technology has drawn a great interest over the last decade because of the following reasons: (i) it can fabricate any kind of 3D structures out of photopolymer based on computer generated 3D model; (ii) the fabrication procedure is rapid and flexible; (iii) the spatial resolution of the structures can be as small as 100 nm; (iv) the fabrication process allows formation of structures directly integrating them into more complex functional micro-devices. There has been a considerable amount of research done by many authors during the last decade revealing the physics of this fabrication technology [1–8].

LTPP is based on quadratic dependence of two-photon absorption rate on light intensity in a photosensitive material. This confines polymerization area to be spatially highly localized at the focal point of a laser beam [3, 4]. By precisely moving sample or beam focus position one can point-by-point solidify the photopolymer. After exposure the rest of the unexposed material is washed out by the solvent during developing process and only the desired structure remains standing free on the substrate.

Recently, a number of this type 3D fabrication experiments were successfully accomplished by applying Ti:sapphire femtosecond lasers generating 800 nm central wavelength light and using commercially available materials such as epoxy based SU-8 photoresins, hybrid organic–inorganic *ORMOCER* materials, and various blends of acrylates [4–8]. LTPP as a fabrication technology could be applicable in areas of micro-optics, photonics, micro-fluidics, micro-opto-electromechanical systems (MOEMS), tissue engineering, etc. [5, 9].

Common LTPP experimental set-ups provide submicrometre resolution and true 3D fabrication possibility,

ISSN 1648-8504

yet are limited to form tiny structures with size of tens or hundreds of microns. For routine application of this technology large fabrication area and high throughput is demanded.

Here, we present a developed LTPP system which enables formation of structures with nanometre resolution and up to millimetre in size. The ability to scale up and speed up the fabrication is offered by slightly modifying focusing optics and adjusting average laser power.

The diameter d and height l of the smallest photopolymerized elements *voxels* (volumetric pixels) can be expressed as [9]

$$d(P_{\mathrm{t}}, t, \mathrm{NA}, \lambda) = \frac{\lambda}{\pi \tan\left(\sin^{-1}\dfrac{\mathrm{NA}}{n}\right)} \times \left\{ \ln \frac{4\pi^2 P_{\mathrm{t}}^2 t \left[\tan\left(\sin^{-1}\dfrac{\mathrm{NA}}{n}\right)\right]^4}{E_{\mathrm{t}}\lambda^4} \right\}^{1/2}, \qquad (1)$$

$$l(P_{\mathrm{t}}, t, \mathrm{NA}, \lambda) = \frac{2\lambda}{\pi \tan^2\left(\sin^{-1}\dfrac{\mathrm{NA}}{n}\right)} \times \left\{ \left[\frac{4\pi^2 P_{\mathrm{t}}^2 t \left[\tan\left(\sin^{-1}\dfrac{\mathrm{NA}}{n}\right)\right]^4}{E_{\mathrm{t}}\lambda^4} \right]^{1/2} - 1 \right\}^{1/2}, \qquad (2)$$

where P and P_{t} are applied average laser power and threshold laser power required for the photopolymerization process, t is exposure time at fixed point, NA is the numerical aperture of the objective, λ is the wavelength in vacuum, n is the index of refraction of the material, and E_{t} is the threshold pulse energy required for photopolymerization. Dynamic range of fabrication is defined as the ratio of the optical damage and photopolymerization threshold power values ($P_{\mathrm{d}}/P_{\mathrm{t}}$). Within the "fabrication window" where the power ranges between P_{t} and P_{d} the voxel size achieved by the femtosecond laser pulses in the photopolymerization process varies with the square dependence on the light intensity. From the theoretical predictions given by (1) and (2) high resolution can be achieved applying lower laser power P and shorter exposure time t. It is seen that voxel dimensions are more sensitive to the change of laser power than to the exposure time. For highest resolution it is important to adjust laser power just slightly above photopolymerization threshold. Thus, laser power stability plays an important role. The NA of the objective lens has a dominant influence on the length of the voxel. It is obvious that shorter wavelength radiation is beneficial for reaching higher resolution due to a smaller diffraction limited spot. Furthermore, two-photon absorption is more efficient in the VIS (VISible) spectral range comparing to NIR (Near Infra-Red) for the most of common photoinitiators.

In our experiment Yb:KGW laser system has been used. Amplified laser system provides high repetition rate (tunable up to hundreds of kHz) and average output power up to 10 W. Frequency doubling of fundamental wavelength provides excitation wavelength to be in the VIS range. That is an advantage, comparing to relatively low repetition rate of Ti:sapphire amplified laser systems operating at few kHz, and a high pulse energy comparing to Ti:sapphire oscillators. High laser average power and high repetition rate is essential for rapid fabrication of micro/nanostructures with overall dimensions of millimetres. The fabricated structures prove that the LTPP system is capable to process various materials required for different applications.

2. Experimental set-up

In our experiments we have used *AltSCA* (*Altechna Co. Ltd.*) positioning system designed for fast and precise laser microfabrication in 3D space for scientific and industrial applications. Amplified Yb:KGW femtosecond laser system *Pharos* (*Light Conversion Co. Ltd.*) with repetition rate 312.5 kHz, average power 6 W, 300 fs pulse duration, 1030 and 515 nm (second harmonic) wavelength laser was used as an irradiation source. The experimental set-up used for LTPP nanostructuring is shown in Fig. 1. The expanded femtosecond laser beam is guided through objective, focusing it into the volume of the photoresin. The sample is mounted on large area XYZ positioning stages. By moving the laser focus inside the photoresin one is able to write complex 3D structures. The CMOS camera enables online process monitoring. The positioning system consists of linear motor driven stages (*Aerotech, Inc.*): *ALS130-150* for XY, *ANT-4V* for Z. These stages ensure an overall travelling range of 150 mm into XY dimensions and 4 mm in Z dimension as well as support sample translation speed up to 300 mm/s. The system can be used for rapid LTPP structuring in various photosensitive materials at large scale with feature sizes as small as 200 nm. The ability to scale up and

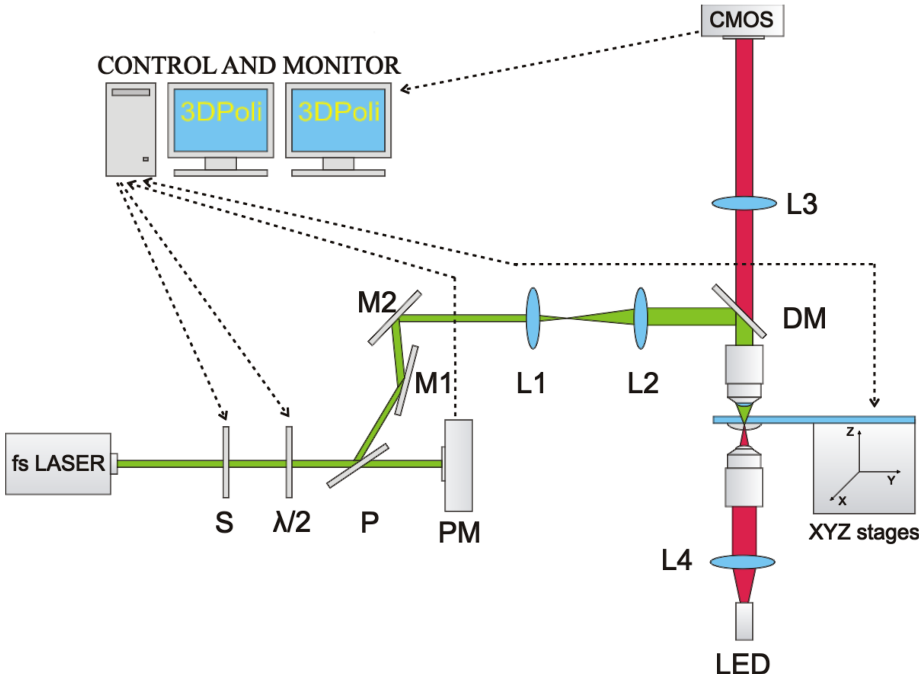

Fig. 1. 3D fabrication set-up. Pulse picker (*S*) is used as a fast and shutter, $\lambda/2$ plate combined with polarizer (*P*) enable control of laser intensity. Mirrors are used for guiding the laser beam, *L1* and *L2* are telescope lenses, *L3* and *L4* serve for illumination optimization and image formation, dichromic mirror (*DM*) transmitting light from light emitting diode (*LED*) enables formation of real time image on CMOS camera, power meter (*PM*) measures average laser power, XYZ stages are used to position the sample.

speed up the fabrication is offered by simply changing the laser beam focusing objective. In this work, we have used several microscope objectives and measured the fabrication resolution. Control of all equipment is automated via *3D-Poli* computer software specially designed for LTPP applications.

3. Materials

In our experiment three different negative photoresins were used. The first material *AKRE19* was composed of commercially available ingredients. Tris (2-Hydroxy ethyl) isocyanurate triacrylate (*SR368*, *Sartomer Company, Inc.*), a polymer that is attractive for its properties like strength without brittleness, low skin irritation, and good chemical adhesion [10], was easily blended with radical photoinitiator thioxanthen-9-one ($C_{13}H_8OS$, *Sigma–Aldrich, Inc.*) [11]. The second material was the organic–inorganic hybrid photopolymer *ORMOCER* (*Micro Resist Technology, GmbH*), a biocompatible photoresin that shows high transparency in the VIS and NIR spectral ranges. *ORMOCER* contains a highly cross-linkable organic network as well as inorganic components resulting in high optical quality and mechanical as well as thermal stability. The polymerization process is initiated by the reaction of the radical photoinitiator (*Irgacure*™ *369*, *Ciba*) [12]. The third photosensitive material is *SU-8* (*Gersteltec Sarl*), widely used in conventional UV lithography. It is an epoxy based photoresin and the cross-linking of molecules is initialized by photoacid generator under light exposure. Under annealing it leads to irreversible cross-linking of the photoresist [13]. *SU-8* is solid during the fabrication, while *ORMOCER* and *AKRE19* are highly viscous liquids. This gives unrestricted freedom in choosing the scanning trajectory of the formed micro-object, comparing to the liquid pre-polymers, where all the details have to be subsequently anchored to the previously formed structures.

4. Results and discussion

In our work, a novel LTPP prototype system has been developed and tested for applications in micro/nanostructuring. For resolution test in *AKRE19* the suspended bridge method was chosen [14]. Suspended lines hanging between solid supporting walls were polymerized using high NA $= 1.25$ oil immersion microscope objective. Structure features were examined by scanning electron microscopy (SEM). In the test structure shown in Fig. 2(a), polymer lines were fabricated using the same scanning speed of 100 μm/s and varying the laser power from below polymerization threshold till microexplosions in pho-

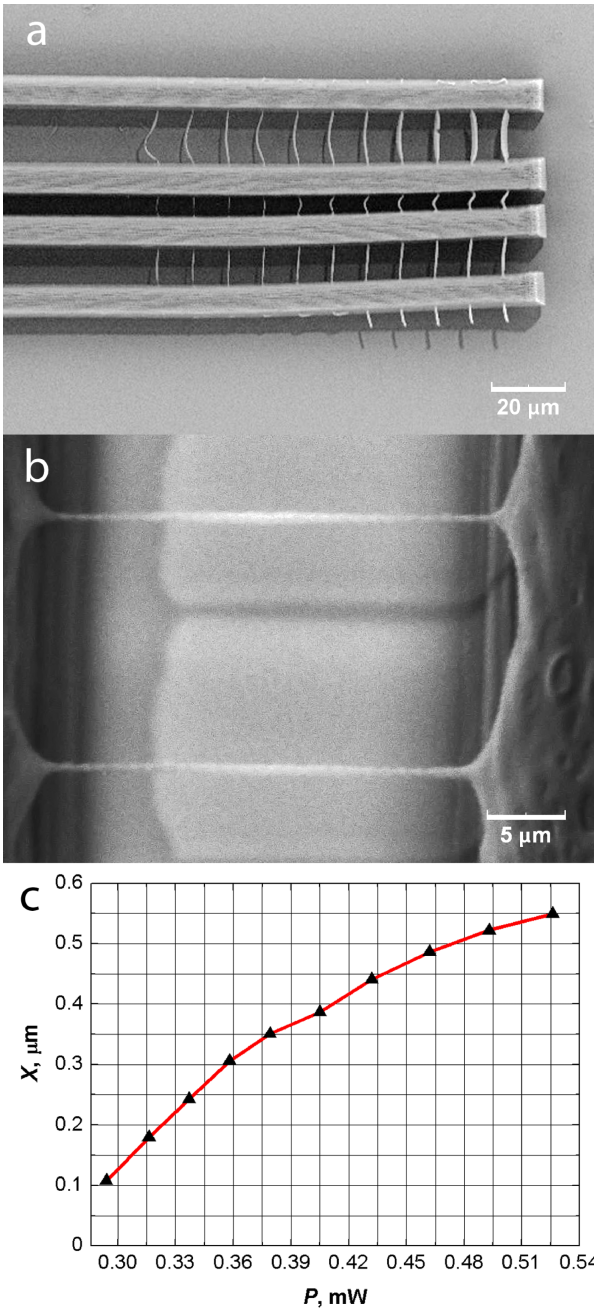

Fig. 2. (a) Suspended bridges for resolution test in *AKRE19* photopolymer. (b) The thinnest robust lines are exhibiting 200 nm lateral resolution. (c) Dependence of lateral line width X on applied average laser power P.

topolymer appeared. The thinnest lines represent highest obtainable resolution, Fig. 2(b). In Fig. 2(c) the resolution dependence on applied laser power graph is shown.

For high resolution and quality structures, such as woodpile geometry photonic crystals, high NA immersion oil objective is necessary and lower scanning speed is preferable, Fig. 3(a). However, large scale structures, e. g. scaffolds for tissue engineering, do not require nanometre resolution. High fabrication speed and larger scale are important in this case. Combination of lower NA optics and higher laser power enables reducing the fabrication time. From Fig. 3 it is seen that 200 nm resolution is achieved with high repeatability and scaling up is realized by changing the focusing objective, sample translation velocity, and laser power.

Table 1. Voxel diameter variation (scaling up) dependence on focusing objectives. M is objective magnification, NA is numerical aperture, X is lateral resolution of a voxel. Minimal and maximal X values obtained experimentally by tuning applied laser power P.

M	NA	X, μm
100	1.25	0.2–0.5
40	0.65	0.4–1
10	0.25	2.5–4.0

Some sample structures were produced for various applications. Woodpile photonic crystal is an example of periodic 3D structure which could be used for photonic devices, Fig. 4(a). Free-hanging chain mail, made of intertwined rings, has high tensile strength and flexibility, Fig. 4(b). These features are important for applications in micromechanics and microfluidics. Comb scaffold, made out of biocompatible *ORMOCER*, is expected to be attractive structure for cell growth experiments in tissue engineering, Fig. 4(c). Self-supporting 3D structure in *SU-8* is example of intricate architecture, Fig. 4(d).

Table 1 shows the voxel lateral size limit dependence on focusing objective. Voxel diameter was changed by tuning laser power, minimal and maximal diameters were estimated from SEM micrographs. It is seen that voxel size varies few times depending on applied laser power and it can be modified significantly by changing the objective. Such resolution tuning can fit different demands for versatile applications.

To calculate time needed for fabrication of a specific structure one can use a simple estimation:

$$\tau \sim \frac{xyz}{R(\mathrm{NA}, P)\, v} F\,, \qquad (3)$$

where τ is fabrication time, x, y, and z are width, length, and height of the structure, R is structuring resolution depending on the NA of the used objective and applied laser power P, v is sample scanning speed, and F is fill factor (the ratio of polymerized versus non-polymerized volume of the whole structure). It is seen that the increase of structure volume dramatically increases the fabrication time as well as fill factor F does. Through changing to appropriate optics and applying high sample scanning velocity it is possible to produce

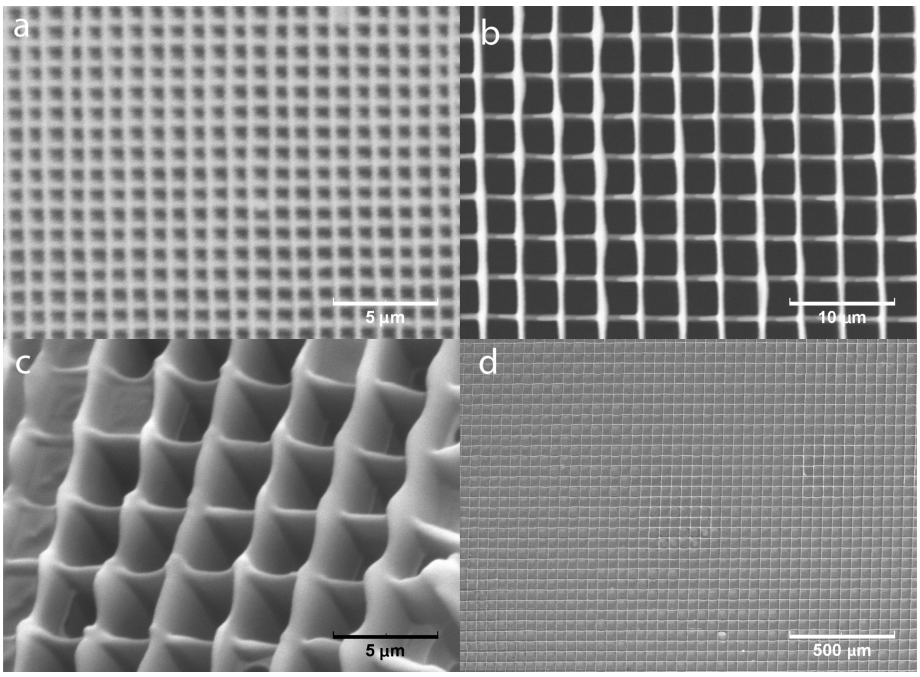

Fig. 3. SEM images of grid structures produced in *AKRE19* photopolymer. Resolution, period, scanning speed, grid size, magnification, and NA of focusing objectives given, respectively: (a) 200 nm, 1 μm, 100 μm/s, 200×200 μm^2, 100×, 1.25, (b) 450 nm, 4 μm, 1 mm/s, 500×500 μm^2, 40×, 0.65, (c) 800 nm, 3 μm, 10 mm/s, 500×500 μm^2, 40×, 0.65, (d) 3500 nm, 50 μm, 100 mm/s, 1.5×1.5 cm^2, 100×, 1.25.

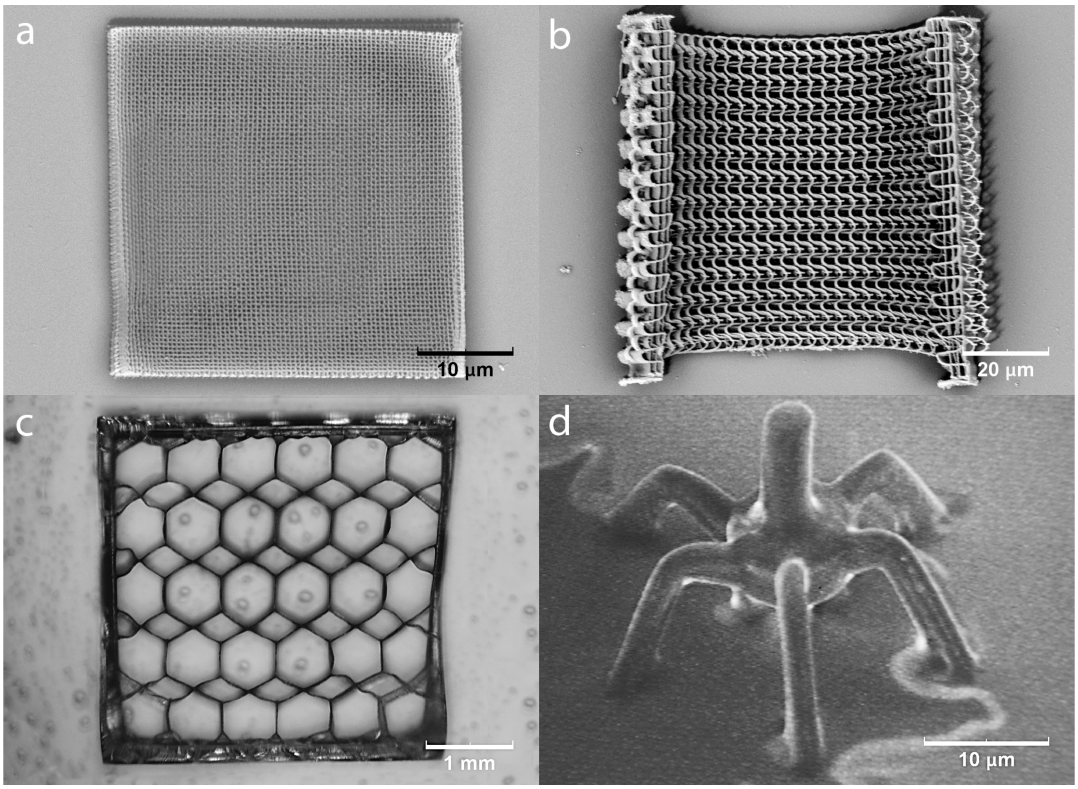

Fig. 4. SEM images of sample structures from various materials. (a) Photonic crystal (woodpile structure) in *AKRE19* photopolymer with 0.5 μm period and resolution 200 nm, structure size 40×40 μm^2, fabrication time 15 min. (b) Free-hanging chain mail in *AKRE19* photopolymer, resolution 400 nm, structure size 80×80 μm^2, fabrication time 15 min. (c) Comb scaffold for cell growth in *ORMOCER* hybrid photopolymer, structure size 4×4 mm^2, fabrication time 30 min. (d) 3D structure in *SU-8* photoresist, fabrication time 20 min.

a relatively large in filled volume structure in less time. For example, fabrication of woodpile structure with lateral and axial period of 8 and 2 μm, respectively, having overall structure size of $800\times800\times40$ μm^3 and roughly 0.5 filling ratio, scanning the sample at 1000 μm/s speed would take just 25 min using a NA $= 0.25$ objective. Using NA $= 1.25$ it would take up to 7 h to fabricate an identical structure. However, if huge volumes are needed to be polymerized and high feature resolution is required, a sophisticated strategy to overcome the drawback of time-consuming fabrication can be invoked. For instance, if a cantilever with a sharp tip is needed, the huge in volume body of the cantilever can be fabricated using a low NA objective and then the sharp tip can be fabricated with a high NA objective. This combination enables fabrication of relatively large (mm in overall scale) volumetric structures with submicrometre feature resolution.

Summarizing, our experiments show that the constructed LTPP system is suitable for rapid micro/nanopatterning of various photoresins and photopolymers which is a requisite for diverse applications in growing demand of miniature functional devices.

5. Conclusion

Nanostructuring for routine fabrication is a complex task. Fast and flexible production, high throughput, easy to operate system, and low maintenance cost, yet high resolution is needed for applications in industry. It is hard to compromise all these requirements at once. High resolution usually correlates with low fabrication speed and small processible area. On the other hand, modification of large area is hardly realized with nanometre resolution or controllable manner. A novel LTPP system, based on high speed wide scanning area linear motor driven stages and high repetition rate Yb:KGW VIS spectral range amplified laser, is offered as a solution. It enables rapid and flexible fabrication of structures with a few hundred nanometres resolution. Furthermore, femtosecond green light capacitates one to produce 3D structures in most of the common photoresins. This sums up the system to be a powerful nanotechnology tool for science and industrial demands. The fabricated sample structures show possible applications in photonics, microoptics, micromechanics, microbiology, and tissue engineering. Though this 3D micro/nanostructuring approach seems a promising prototype for mass production, it still can be further upgraded. The excess of laser power can be used for parallel beam processing in order to increase the fabrication throughput. An integration of additional OPA (optical parametric amplifier) would provide irradiation wavelength tuning from UV to NIR, which would extend the variety of processible materials and fabrication efficiency. Techniques for two-colour processing could lead to collateral increase of fabrication resolution as well.

Acknowledgements

This work is supported by the Lithuanian State Science and Studies Foundation grant B09/08 (Laser Micro-processing With High Repetition Femtosecond Pulses – FEMTOPROCESSING). In addition, authors would like to thank *Sartomer Company, Inc.* for providing materials for the experiments. Lastly, authors are grateful to Dr. A. Ovsianikov (Nanotechnology Department, Laser Zentrum Hannover, Hannover, Germany) for fruitful discussions.

References

[1] S. Wu, J. Serbin, and M. Gu, Two-photon polymerisation for three-dimensional micro-fabrication, J. Photochem. Photobiol. A **181**(1), 1–11 (2006).

[2] S.H. Park, K.H. Kim, T.W. Lim, D.Y. Yang, and K.S. Lee, Investigation of three-dimensional pattern collapse owing to surface tension using an imperfection finite element model, Microelectron. Eng. **85**, 432–439 (2008).

[3] S. Kawata, H.B. Sun, T. Tanaka, and K. Takada, Finer features for functional microdevices, Nature **412**, 697–698 (2001).

[4] S. Juodkazis, V. Mizeikis, K.K. Seet, M. Mima, and H. Misawa, Two-photon lithography of nanorods in SU-8 photoresist, Nanotechnology **16**, 846–849 (2005).

[5] B.N. Chichkov, J. Koch, A. Ovsianikov, S. Passinger, C. Reinhardt, and J. Serbin, Direct-write micro- and nanostructuring with femtosecond lasers, Mater. Res. Soc. Symp. Proc. **850**, 251–258 (2005).

[6] L. Li and J.T. Fourkas, Multiphoton polymerization, Mater. Today **10**(6), 30–37 (2007).

[7] W. Haske, V.W. Chen, J.M. Hales, W. Dong, S. Barlow, S.R. Marder, and J.W. Perry, 65 nm feature sizes using visible wavelength 3-D multiphoton lithography, Opt. Express **15**(6), 3426–3436 (2007).

[8] M. Farsari, G. Filippidis, and C. Fotakis, Fabrication of three-dimensional structures by three-photon polymerization, Opt. Lett. **30**(23), 3180–3182 (2005).

[9] K.-S. Lee, R.H. Kim, D.-Y. Yang, and S.H. Park, Advances in 3D nano/micro-fabrication using two-photon initiated polymerization, Progr. Polymer Sci. **33**, 631–681 (2008).

[10] www.sartomer.com/proddetail.asp?plid=1&sgid=4&prid=SR368 (2008-07-09).
[11] www.sigmaaldrich.com/Area_of_Interest/Chemistry/Materials_Science/Polymerization_Tools/Initiators.html (2008-07-10).
[12] www.microresist.de/poster_ormocer.pdf (2006-05-13).
[13] www.microchem.com/products/pdf/SU8_2002-2025.pdf (2007-05-04).
[14] H.B. Sun and S. Kawata, Two-photon photopolymerization and 3D lithographic microfabrication, in: *NMR. 3D Analysis. Photopolymerization*, Adv. Polymer Sci. **170**, 169–273 (2004).

FEMTOSEKUNDINIAIS REGIMOSIOS ŠVIESOS IMPULSAIS INDUKUOTOS DVIFOTONĖS POLIMERIZACIJOS PANAUDOJIMAS TRIMAČIAMS MIKRO- AR NANODARINIAMS FORMUOTI FOTOREZISTUOSE IR FOTOPOLIMERUOSE

M. Malinauskas, V. Purlys, M. Rutkauskas, A. Gaidukevičiūtė, R. Gadonas

Vilniaus universitetas, Vilnius, Lietuva

Santrauka

Lazerinė dvifotonė fotopolimerizacija (LDFP) – unikali technologija, naudojama trimačiam mikro- ar nanostruktūrizavimui. Toks femtosekundiniais lazeriais paremtas tiesioginis rašymas leidžia pasiekti mažesnę už bangos ilgį objektų formavimo skyrą. Pristatoma sukonstruota LDFP sistema, panaudojant didelio darbinio lauko ($150\times150\times4$ mm^3) ir skenavimo greičio (iki 300 mm/s) bandinio pozicionavimo stalus ir aukšto pasikartojimo dažnio (312,5 kHz) Yb:KGW lazerio spinduliuotės antrąją harmoniką (515 nm) kaip šviesos šaltinį. Ja sparčiai ir atkartojamai galima formuoti nanodarinius 200 nm skersine skyra. Keičiant lazerio pluošto fokusavimo optiką, galima derinti ir optimizuoti tokio formavimo tikslumą bei našumą. Tai leidžia gaminti milimetrinių matmenų trimačius darinius, kurie gali būti taikomi mikrooptikoje, fotonikoje, mikrohidrodinamikoje, audinių inžinerijoje ir kitur. Tam galima naudoti įvairias UV litografijoje naudojamas fotojautrias medžiagas (akrilatus, hibridinius organinius–neorganinius polimerus, epoksidines dervas). Visa tai leidžia sukurtą LDFP sistemą efektyviai naudoti sparčiam ir lanksčiam palyginus didelių matmenų mikro- ar nanodarinių formavimui.