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High-speed two-photon polymerization 3D printing with a microchip laser at its fundamental wavelength

DMITRII PEREVOZNIK,[1,2] RASHID NAZIR,[3,4] ROMAN KIYAN,[1,2,6] KESTUTIS KURSELIS,[1] BEATA KOSZARNA,[3] DANIEL T. GRYKO,[3,7] AND BORIS N. CHICHKOV[1,2,5]

[1]*Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover, Germany*
[2]*Cluster of Excellence PhoenixD (Photonics, Optics, and Engineering – Innovation Across Disciplines), Hannover, Germany*
[3]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44-52, 01-224 Warsaw, Poland*
[4]*Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland*
[5]*Lebedev Physical Institute, Leninsky Prospect 53, 119333 Moscow, Russia*
[6]*roman.kiyan@lnqe.uni-hannover.de*
[7]*dtgryko@icho.edu.pl*

Abstract: High-resolution, high-speed 3D printing by two-photon polymerization (2PP) with a Nd:YVO_4 Q-switched microchip laser at its fundamental wavelength of 1064 nm is demonstrated. Polymerization scan speeds of up to 20 mm/s and feature sizes of 250 nm are achieved using a high repetition rate Q-switched microchip laser with a semiconductor saturable absorber mirror (SESAM) and photoresist with a new photo-initiator bearing 6-dialkylaminobenzufuran as electron donor and indene-1,3-dione moiety as electron acceptor. The obtained results demonstrate the high potential of Q-switched microchip lasers for applications in 2PP 3D printing.

1. Introduction

Laser additive manufacturing is a rapidly growing technology, with an increasing impact in modern industry [1]. Various functional materials, including polymers, metals, glasses and ceramics, can be 3D printed with the help of laser radiation [2]. Laser technologies are also allowing 3D printing with an unmatched sub-micrometer resolution. Routinely, spatial resolution down to 100 nm is achievable by applying the two-photon polymerization (2PP) technology [3–5]. This technology is used for direct writing of complex three-dimensional objects without any geometrical limitations [6] as opposed to stereo-lithography, where 3D printing is done layer by layer [7]. 2PP based 3D printing has already been used for various applications, including fabrication of photonic elements, micro-electro-mechanical systems (MEMS), microfluidic components, and fabrication of scaffolds for regenerative medicine [8–12]. However, industrial applications of 2PP 3D printing are limited since the current 2PP technology relies on femtosecond lasers that are expensive, complex, and sensitive to the environment. In the efforts to simplify and industrialize the direct laser writing of 3D polymer structures by 2PP, approaches using CW solid-state laser [13] and UV laser diode [14] have also been examined. However, in both these papers, well characterized 2D fabrication on a substrate surface is very slow (in the range of 0.1–0.2 mm/s) and data on more challenging 3D writing are missing. Consequently, to the best of our knowledge, there are no published reports on the application of these lasers for industrial 3D printing. From currently available laser alternatives, Q-switched microchip lasers with Nd-doped crystalline active media [15] are very attractive light sources for 2PP 3D printing. Thanks to the application of highly

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doped, high gain media, microchip lasers can be extremely compact, maintenance-free, and sufficiently cheap for mass-production.

The first attempts to utilize Q-switched microchip lasers for 2PP [16] reported results which were inferior to that achieved with femtosecond lasers. This is partially due to the characteristics of commercially available Q-switched microchip lasers that are not optimal for the 2PP process. Typically, microchip lasers generate sub-nanosecond pulses with the pulse energy of few microjoules and repetition rate below 50 kHz [17–19]. In addition, as the available photoresist-photoinitiator systems are not sufficiently sensitive to the radiation of Nd-doped Q-switched microchip lasers at the fundamental wavelength of 1064 nm, the second harmonic was applied for 2PP [18,19] resulting in additional complication of the laser system and reduced energy efficiency. Reliable photoresists for 2PP 3D printing at 1064 nm wavelength still have not been developed despite the reported attempts [20].

In this paper, significant improvements of the 2PP 3D printing quality and performance by using a Q-switched microchip laser are reported. This laser is based on a special microchip cavity with a semiconductor saturable absorber mirror (SESAM) bonded to a Nd:YVO_4 crystal [21]. This layout enabled the generation of picosecond laser pulses at the repetition rate of several hundred kHz. Thanks to the laser performance and high 2PP reactivity of the prepared photoresist directly at the fundamental wavelength of our microchip laser, 2PP 3D printing speeds of up to 20 mm/s are demonstrated and objects with feature sizes down to 250 nm are produced. These 2PP 3D printing characteristics are on par with femtosecond lasers.

2. Materials and methods

To improve the 2PP process, a recently synthesized photoinitiator based on an α,β-unsaturated 1,3-diketone [22] was used (Fig. 1(a)). The usage of ketones as initiators of both single- and two-photon polymerization is ubiquitous [23–26]. The carbonyl group being one of the strongest electron-withdrawing groups, offers obvious advantages in the design of organic dyes possessing large two-photon absorption. Moreover, conjugated 1,3-diketones possess even stronger electron-withdrawing effects [27,28]. In order to shift the one-photon absorption (and hence two-photon absorption) bathochromically the design of new photoinitiator implied the combination of 6-dialkylaminobenzofurane (one of the strongest, aromatic electron-donating moieties) and indene-1,3-dione (one of the strongest acceptors). As a result of this structural engineering the dye absorbs at 520 nm (Fig. 1(b)), which given its dipolar D-π-A architecture should lead to strong two-photon absorption at ~1040 nm. Initial two photon absorption assessment of the synthesized photoinitiator is reported in [22]. The dye is highly transparent in the NIR with only background absorption (see inset in Fig. 1(b)). The additional crucial aspect of our design is the presence of long alkyl chains which secures very good solubility of the ketone in various media.

Figure 2 shows the applied 2PP 3D printing setup. The microchip Q-switched laser was build using a Nd:YVO_4 microchip with attached SESAM that is commercially available from BATOP GmbH (Germany). A temperature stabilized laser diode pigtailed with a multimode optical fiber (50 µm core diameter, NA = 0.22) was used as a pump source at 808 nm. Pump radiation from the optical fiber was collimated and, after passing through a polarizer, focused on the dichroic mirror deposited directly on the back surface of Nd:YVO_4 microchip. A SESAM is attached to the front surface of the microchip and serves as a saturable absorber and output mirror. The size of the pump beam focal spot at the microchip surface is approximately 40 µm.

The microchip laser generates pulses at 1064 nm with a pulse energy of 95 nJ and pulse duration of 90 ps. The pulse repetition rate of 330 kHz, that was achieved at 300 mW pumping power, is used in all our polymerization experiments. Output of the microchip laser is collimated to a beam with the diameter of 4.5 mm. The microchip laser was installed into M4D Micro and Nano Structuring system (Laser nanoFab GmbH, Germany). The laser beam

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power applied for 3D printing is adjusted with a half-wavelength wave plate and a polarization beam splitter. Finally, the beam is directed to a 40x microscope objective with NA = 0.65 (Zeiss, Germany) to focus laser radiation in the volume of a photoresist. The transmission of the microscope objective at the laser wavelength is of about 0.75.

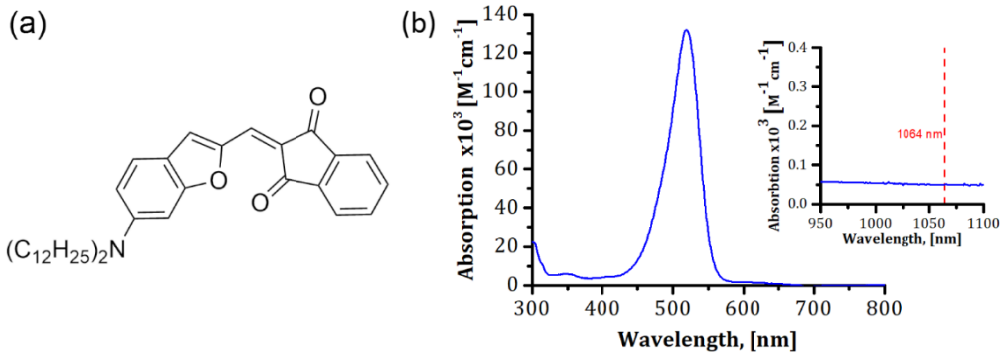

Fig. 1. The structure of the photoinitiator (a). Single photon absorption spectrum of the photoinitiator (in dichloromethane) (b). Absorption spectrum in the vicinity of laser wavelength is shown in the inset (in acetone).

The photoresist was prepared by adding the indene-1,3-dione containing photoinitiator to a Zr-based organic-inorganic hybrid material [29]. The photoinitiator was dissolved directly in the organic-inorganic material in a concentration of 1%wt. Samples were made by dropcasting the photoresist on the surface of a 150 μm thick glass slide and pre-baked on a hot plate at 40°C for 180 min as it was explained in [29]. For 2PP microstructuring they were fixed to the high precision air-bearing horizontal X-Y positioning stage of the M4D Micro and Nano Structuring system, whereas the microscope objective was mounted on a vertical air-bearing Z-positioning stage. The laser beam focal spot was scanned in the volume of the photoresist by computer controlled motion of these stages.

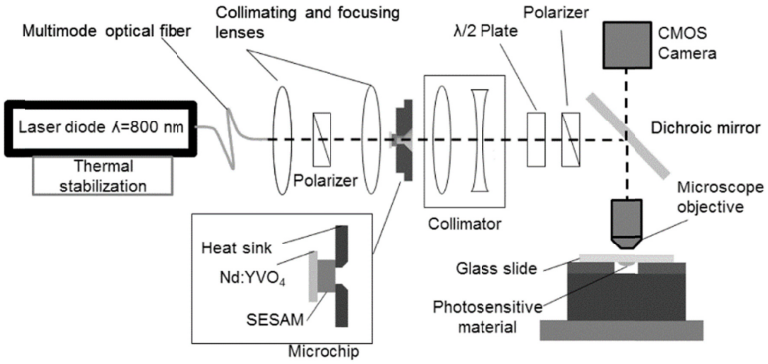

Fig. 2. Experimental setup for two-photon polymerization with the Q-switched microchip laser.

After the 2PP fabrication process, samples were post-baked on a hot plate at 100°C for 60 min in order to improve adhesion of the polymeric structures to the glass substrate. Then, non-polymerized material was washed out by dipping the samples in 1-propanol for 60 s, leaving only the laser irradiated material on the glass slide with a high resolution 3D microstructure.

In order to characterize 2PP 3D printing of the applied photoresist by Q-switched microchip laser, 3D woodpile structures were fabricated with different laser spot scanning speeds and laser powers.

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3. Results

Scanning speeds in the range of 0.1 mm/s to 20 mm/s and average laser powers in the range of 5 mW to 30 mW were investigated. Low scan speed and/or high laser power result in damage to the woodpiles due to overexposure. Underexposure, due to high scan speeds or low laser power, lead to mechanically unstable structures which are partly washed away in the development process. The scan speeds and laser powers which result in non-damaged, stable structures define the 2PP process window in the two-dimensional parameter space. On the speed dimension, the structuring window spans as far as to 20 mm/s and is limited only by the available laser power. The smallest feature size of about 250 nm was achieved with all examined scanning speeds by choosing laser power close to the polymerization threshold.

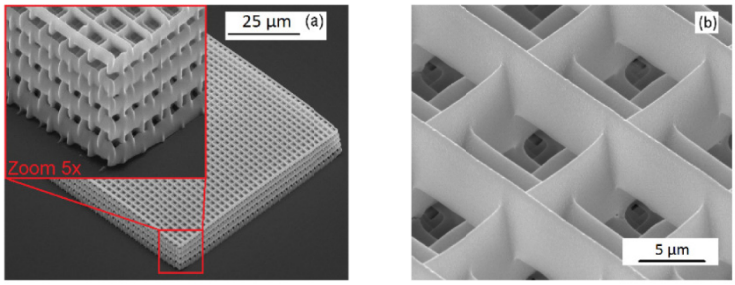

Fig. 3. SEM images of 3D woodpile structures fabricated by the SESAM Q-switched microchip laser: (a) - average laser power of 17 mW and scanning speed of 0.6 mm/s; (b) - average laser power of 27 mW and scanning speed of 19 mm/s.

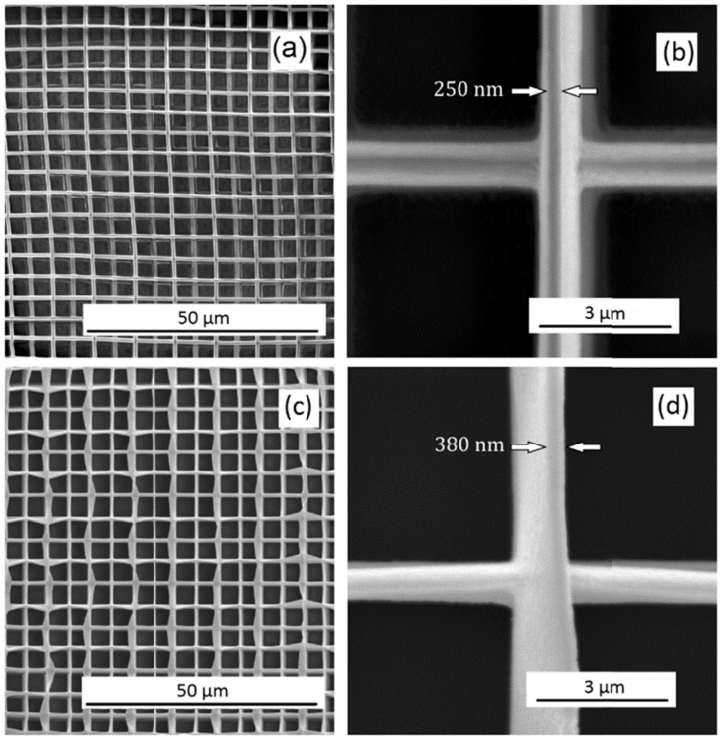

Fig. 4. SEM images of 3D woodpile structures demonstrating the ultimate achieved feature size and fabrication speed: (a), (b) - woodpile structure fabricated with average laser power of 14 mW and scanning speed of 5 mm/s; (c), (d) - woodpile structure fabricated with average laser power of 27 mW and scanning speed of 20 mm/s.

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Polymerization of the Zr-based organic-inorganic hybrid material without adding the photoinitiator was also attempted. No microstructures could be produced in the accessible power range and scan speeds. This result indicates that under the relevant experimental conditions purely thermal polymerization was not possible and two-photon absorption by the photoinitiator was a primary mechanism of the polymerization.

Examples of scanning electron microscope (SEM) images of the fabricated 3D woodpile structures are shown in Fig. 3. SEM images, illustrating the ultimate achieved feature size and fabrication speed are shown in Fig. 4 for the two scanning speeds of 5 mm/s and 20 mm/s with 14 mW and 27 mW average laser powers, respectively. The demonstrated smallest feature size of 250 nm is well beyond the diffraction limit and can be further improved by using a microscope objective with higher NA at 1 μm wavelength.

Relatively low NA of the used objective, which was chosen due to the lack of available alternatives optimized for 1064 nm, resulted in producing of narrow (~250 nm) and tall (several μm) polymeric rods (Fig. 3(b)). Correspondingly, due to the achieved high aspect ratio (> 10), some of the top layer polymeric rods tend to flex sideways as in Fig. 4.

In order to investigate the achievable feature sizes, widths of the polymeric rods forming the woodpile structures obtained at different scanning speeds and laser powers were measured. These measurements were carried out using magnified SEM images of the woodpiles.

The experimentally measured data of the polymeric rods width were fitted using the analytical expression for the 2PP voxel diameter [4]:

$$d\left(N_0, t\right) = r_0\sqrt{\ln\left(\sigma_2 N_0^2 n\tau / C\right)} \tag{1}$$

where σ_2 is the effective two-photon polymerization cross section; $C = \ln\left[\rho_0/\left(\rho_0 - \rho_{th}\right)\right]$ with the primary initiator molecule density ρ_0 and polymerization threshold density of radicals ρ_{th}; τ is the laser pulse duration; the light distribution at the focal plane is assumed to be Gaussian: $N(r) = N_0 \exp\left(-2r^2/r_0^2\right)$ with HW e^{-2} denoted as r_0. The relationship between the photon flux N_0 and average laser power P is $N_0 = 2PT/\pi r_0^2 \tau \nu \hbar\omega$, where T is the transmission of the microscope objective at the laser optical frequency ω; ν is the laser pulse repetition rate.

The number of applied laser pulses per voxel is $n = \nu t$, where t is the voxel exposure time. The exposure time depends on the scanning speed V and is estimated by $t = 2r_0/V$.

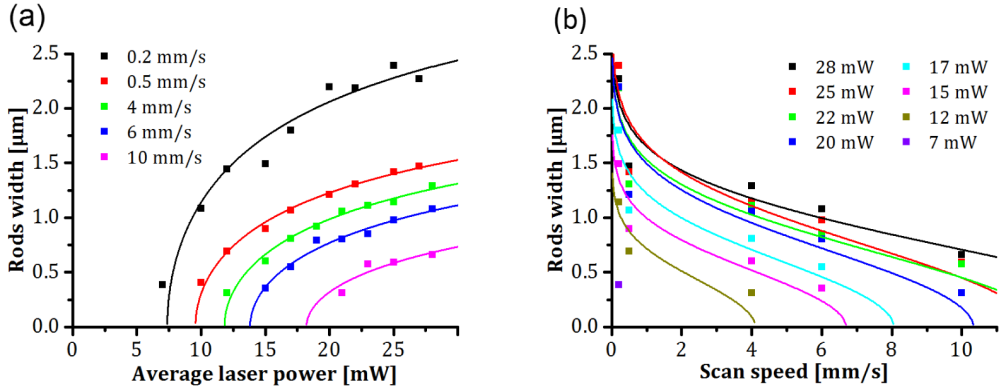

Fig. 5. Experimental dependencies of the width of the polymeric rods produced by 2PP with a microchip SESAM Q-switched laser on average laser power (a) and laser spot scanning speed (b). Fitting curves obtained with [Eq. (1)] are shown by continuous lines.

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The experimental results and the voxel diameter fitting curves obtained using [Eq. (1)] are shown in Fig. 5. The experimental results obtained with the SESAM Q-switched microchip laser are consistent with that reported for 2PP by a femtosecond laser [4]. Fitting of the data enables the determination of the polymerization threshold power for each scanning speed as well as the highest possible scanning speed for each of the examined powers.

The fitting applied to each experimental dependence measured at different experimental conditions is resulting in two fit parameters $\sigma_{eff} = \sigma_2 T^2 / C$ and r_0 for each curve. Mean value of the fitting parameter σ_{eff} is $(2.2 \pm 0.3) \cdot 10^{-51}$ cm^4 s. Results obtained for the polymeric rods width dependencies on average power and scan speed are summarized in Fig. 6. Although, the same value of the parameter r_0 could be expected for all dependencies in Fig. 5, it is actually different. Such a behavior was already reported in [30]. This discrepancy with theoretical model [4] is explained by the accumulation and diffusion of heat [30], light scattering and additional free radicals generation in the photoresist.

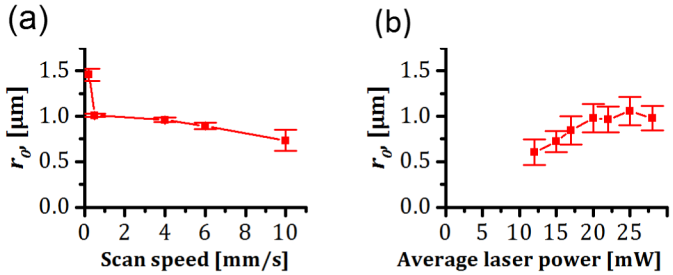

Fig. 6. The fit parameter r_0 for the polymeric rods width dependencies on average laser power (a), corresponding to Fig. 5(a), and scan speed (b), corresponding to Fig. 5(b).

4. Conclusion

A high performance microchip laser, based on a Nd:YVO_4 SESAM Q-switched cavity at its fundamental wavelength of 1064 nm, was applied for two-photon polymerization of a hybrid photoresist using an indene-1,3-dione containing photoinitiator. Polymerized feature sizes of down to 250 nm and polymerization speeds of up to 20 mm/s have been achieved. Both, the feature sizes [4] and polymerization speeds [31] are on a par with 2PP fabrication by femtosecond lasers, with a significant reduction in the system footprint and cost.

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