Title	Refractive femtosecond laser beam shaping for two-photon polymerization
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Publication date	2007
Original citation	Winfield, R. J., Bhuian, B., O'Brien, S. and Crean, G. M. (2007) 'Refractive femtosecond laser beam shaping for two-photon polymerization', Applied Physics Letters, 90(11), pp. 111115. doi: 10.1063/1.2713787
Type of publication	Article (peer-reviewed)
Link to publisher's version	http://aip.scitation.org/doi/abs/10.1063/1.2713787 http://dx.doi.org/10.1063/1.2713787 Access to the full text of the published version may require a subscription.
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Item downloaded from	http://hdl.handle.net/10468/4382

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Citation: Appl. Phys. Lett. **90**, 111115 (2007); doi: 10.1063/1.2713787
View online: http://dx.doi.org/10.1063/1.2713787
View Table of Contents: http://aip.scitation.org/toc/apl/90/11
Published by the American Institute of Physics

Refractive femtosecond laser beam shaping for two-photon polymerization

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(Received 14 November 2006; accepted 10 February 2007; published online 15 March 2007)

Three dimensional microstructure fabrication by two-photon polymerization is an established technique that normally uses single beam serial writing. Recently the use of a micro-optical element, to give multipoint beam delivery, was reported to give a degree of parallel processing. The authors describe an alternative approach to parallel processing using an axicon lens. This is a refractive element that, in combination with a high power microscope objective, efficiently transforms the laser beam from a Gaussian spot to an annulus. The authors demonstrate that the beam can polymerize a three dimensional shape, with nanoscale resolution. The use of more sophisticated refractive beam shaping is also discussed. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2713787]

Conventional two-photon polymerization (2PP) has demonstrated a rapid nano-scale fabrication technique with resolution in the region of 100 nm.[1–3] The interaction volumetric pixel (voxel) is much smaller than any produced by single-photon absorption due to the dependence of the photoinitiator absorption on the square of the laser beam intensity. In addition, there is a threshold for the polymerization process and this can be utilized in order to reduce the effective diameter of the Gaussian focal spot by ensuring that the low intensity wings of the laser intensity distribution are below this threshold.[3] Using this technique, complex shapes such as micromodels, woodpile photonic structures and spiral structures, have been realized in several material systems: sol gels, organically modified ceramics, and resins.[1,3–5]

Traditionally the fabrication process is a serial writing technique where the voxel is scanned through the volume of the material as a series of curved or straight lines. A high numerical aperture (NA) microscope objective (typical NA >1.0) is used as the focusing element. Recently multipoint processing by splitting the beam into an array of beamlets, each of which is brought to a focus in the material, has been demonstrated. Kato *et al.*,[6] using an amplified Ti:sapphire laser source (1.8 mJ/pulse, 1 kHz pulse repetition rate), simultaneously wrote up to 227 structures with an array of refractive microlenses. Winfield *et al.*[7] used a Ti:sapphire oscillator (10 nJ/pulse, 80 MHz pulse repetition rate) with a diffractive optical element to simultaneously write four lines in a grating structure. In each case, an *XYZ* stage system was required to form the pattern.

In this letter we describe an alternative technique to achieve parallel processing, namely, the use of a refractive optic to shape the beam at the interaction plane. A schematic diagram of the experimental arrangement is shown in Fig. 1. It comprises a 100 fs pulse width Ti:sapphire laser (Spectra Physics Mai Tai) of wavelength of 790 nm, pulse repetition rate of 80 MHz, and average power of 700 mW (measured at the laser).

A sol-gel resin was used as the medium for writing the structures. A precursor containing 5 mol % Zr was prepared by hydrolysis of an organosilane to which a chelated zirconium alkoxide was added.[5] Water was then added to promote condensation reactions between hydrolyzed precursors and a photoinitiator species was added immediately prior to deposition. The photoinitiator (2.0% by weight) 4,4′-bis(diethylamino) benzophenone was chosen for its high absorption cross section at 400 nm. The sol gel was dipped onto glass substrates 170 μm thick, allowed to dry, and mounted inverted onto a motorized *XYZ* stage system. In order to maintain the high numerical aperture of the objective, index matching fluid was used between the objective and the substrate. The polymerization process was observed via a charge coupled device (CCD) camera.

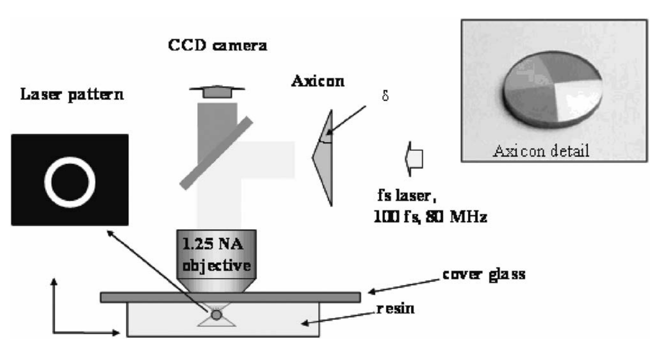

FIG. 1. 2PP system comprising femtosecond laser oscillator, high NA objective index matched into the resin system. An axicon lens is included to modify the laser intensity pattern at the focal plane of the objective.

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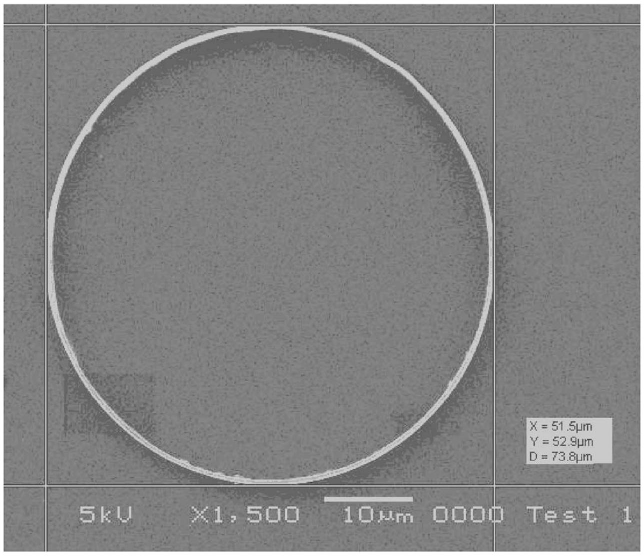

FIG. 2. Plan view of a three dimensional annular shape polymerized in a single 2.5 s exposure.

The experimental system reported in this letter differs from the standard arrangement for 2PP by the introduction of an axicon refractive element; essentially a conical pyramid with base angle (δ) of 2 degrees (see insert of Fig. 1). The axicon transforms the quasiparallel Gaussian beam output of the laser into an expanding annulus of light. To initiate polymerization, the diameter of the annulus is reduced by a focusing element. With this process a complete three dimensional annular volume can be polymerized without the use of computer numerical control (CNC) stage control in the *XY* plane.

An oil immersion 100× microscope objective with a numerical aperture of 1.25 was used. The effective focal length of the objective (f) was 1.6 mm. The outer diameter (d) of the annulus at the focal plane of the objective is given by an elementary application of Snell's law: $d=2f\tan\{\delta(n-1)\}$. In our system, where the refractive index of the axicon (n) was 1.507, the calculated diameter was 54 μm.

The thickness (t) of the annulus was more difficult to estimate. The upper limit bound is given by the intrinsic divergence of the expanded laser beam θ (estimated to be 0.5 mrad) from $t=f\theta$, giving a thickness of 0.8 μm. However, this will be modified by both two-photon and threshold effects and also by experimental factors such as laser pointing stability.

Figure 2 shows a representative annulus formed by this technique. The average diameter of the annulus, measured using a Hitachi S4000 SEM, was 52.2 μm. The shape is circular to within ~3%. The exposure was 2.5 s at an average laser power (measured at the back aperture of the objective) of 300 mW. Following the exposure step, the unpolymerized material was removed by dissolution in isopropyl alcohol to leave the solid annulus. This sol-gel material was previously shown to polymerize by 2PP under femtosecond laser irradiation, leaving a stable structure without the need for postprocessing.

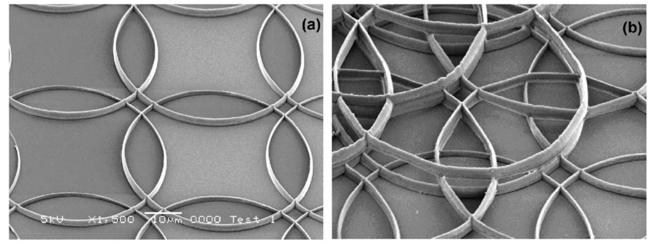

FIG. 4. Complex patterns built up by a step-and-repeat process using the basic annular shape: (a) single layer and (b) stacked layers.

In a typical standard 2PP polymerization process, where the laser is focused into a small voxel, the resulting polymerization volume is aspherical with the vertical dimension larger than the horizontal. For the same optical focusing characteristics (lens focal length, numerical aperture, laser beam) the dimensions are dependent on the laser dosage. In this experiment the laser power was constant and therefore the dosage was proportional to the exposure time.

Figure 3 shows the height and width of the annulus wall for a range of exposure times. It is observed that the dimensions of the polymerized volume increase with exposure, as in the case of a point focus system. The aspect ratio of the annulus wall (height compared to width) also shows a similar trend to voxels measured using single point processing.[8]

The use of the axicon does not preclude the possibility of building up more complex patterns based on the annular shape. Figure 4(a) shows a single layer pattern of interlocking annuli. It is observed that the quality of the intersections is good. The tilted view shows clearly the height and width difference studied in Fig. 3. Very little interference is seen between the overlapping structures.

One of the advantages of the 2PP process is that the photoinitiator has a very low absorption cross section at the laser wavelength. Therefore, the 2PP process can occur at any point within the sol gel. This allows an annular pattern to be stacked into larger structures. Figure 4(b) shows annular structures repeated in three dimensions. A circular base unit

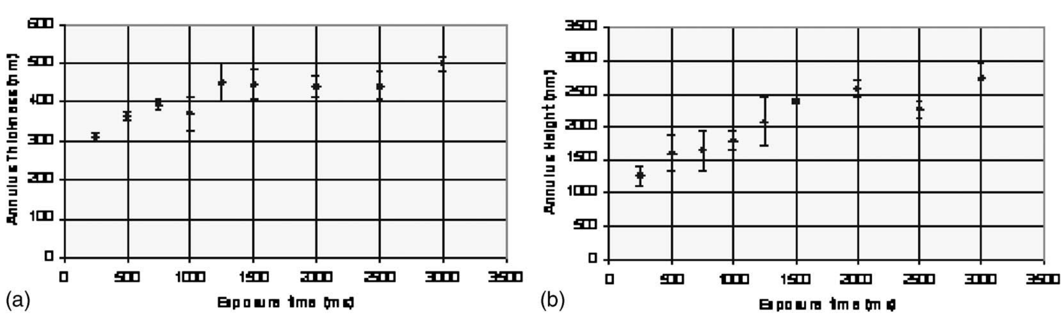

FIG. 3. 3D polymerization characteristics: (a) height and (b) width of the annulus wall as a function of exposure time for constant average laser power.

lends itself conveniently to the formation of unit cells with hexagonal symmetry. The ability to form these complex three dimensional (3D) patterns could pave the way to building hexagonal photonic crystals,[9,10] cell scaffolds,[11] etc.

In conclusion, it is demonstrated that an axicon lens can be used in a 2PP system to polymerize a complex shape. This avoids the use of sophisticated *XY* stage control. It is shown that parallel processing using a refractive beam-shaping element is an attractive method for the fabrication of an annular structure. The resolution achieved is excellent and polymerized widths of 300 nm were measured in a 50 μm diameter shape. Using a step-and-repeat technique, more complex two dimensional and 3D structures can be constructed.

Furthermore, with this technique, the polymerized shapes are not restricted to annuli. For example, a tetrahedral pyramid could be used, as a refractive element instead of the axicon, to produce a 2×2 array of focused spots. Specifically, designed optical surfaces with more complex refractive forms could be used to generate arbitrary patterns at the focal plane of the objective (see, for example, Schilling *et al.*[12]). The use of refractive optics in the modification of the focused laser beam profile is therefore a powerful technique for the development of future micro-/nanostructures.

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