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# Two-photon polymerisation of novel shapes using a conically diffracted femtosecond laser beam

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ABSTRACT

Sub-micron ring, pillar and wall structures were written by two-photon polymerisation of a sol–gel resin using a femtosecond laser beam which was shaped using internal conical diffraction. The ring structure was written using a demagnified image of the ring-shaped beam which arises in conical diffraction of a narrow light beam. The pillar and wall structures were produced by imaging the Bessel beam formed by conical diffraction in combination with a converging lens.



## 1. Introduction

Two-photon polymerisation (TPP) of liquid and sol–gel resins with femtosecond (fs) lasers is now widely used for fabrication of a wide range of three-dimensional structures with sub-micron critical dimensions [1]. Since TPP relies on two-photon absorption (TPA), the rate of polymerisation depends on the square of the light intensity, and thus it is possible to achieve higher spatial resolution than with a single photon absorption process [1,2]. For some applications of TPP, such as writing wall structures, the process efficiency can be improved if the focussed laser beam has a large depth of focus, such as in a zero order Bessel beam. In that case polymerisation occurs simultaneously at different depths without the need to translate the focal point or the sample along the beam axis [3]. The formation of a Bessel beam requires an optical setup which produces a conical superposition of wave-fronts. The zero order Bessel beam comprises a central spike surrounded by concentric rings, with the property that the optical power in each ring is equal [5,6]. For the zero order Bessel beam the overall optical power can be chosen such that there is negligible TPA in the rings as compared to the on-axis spike. In Ref. [3] the zero order Bessel beam was formed using an axicon and was imaged with a high power optical objective into the resin to write microwires. By laterally translating the sample in the Bessel region, wall and grid structures with wall thickness of 1 μm and wall height of 20 μm were written [4]. In the focal plane of the objective the Bessel beam is transformed to a narrow ring; this was used to write thin ring-shaped structures.

Internal conical diffraction (ICD) offers an alternative method for the transformation of a Gaussian beam to a Bessel beam. In conical diffraction a beam of light which is incident along one of the optic axes of a biaxial crystal propagates as a hollow cone of rays inside the crystal and emerges with a double-ringed profile [7–9]. This conically diffracted beam can be used to form both weakly-diverging and non-diverging zero and first order Bessel beams [9]. In fact, ICD of a Gaussian beam without a converging lens produces a superposition of diverging zero and first order Bessel beams, each carrying equal optical power when the radius of the double-ring is large compared to the Gaussian beam waist [8]. For a circularly polarised input beam, the zero order beam has the same polarisation as the input, while the first order beam is orthogonally polarised. In this paper we describe the results of an experiment where TPP was carried out using a Bessel beam formed by conical diffraction. Ring, pillar and grid structures, with sub-micron dimensions, were prepared.

## 2. Experiment

The optical setup used to form the Bessel beam and image it into resin is shown in Fig. 1. The optical source used was a 100 fs Ti:sapphire laser (Spectra Physics Mai Tai) operating at 795 nm. The repetition rate was 80 MHz and the average power output was 750 mW. A converging lens $L_1$ with focal length $f_1 = 10$ cm was used to focus the laser beam to a Gaussian spot with a $1/e^2$ radius $\omega = 50$ μm. The biaxial crystal was placed between the lens and the beam waist to minimise the optical intensity in the crystal. The crystal acts to transform the Gaussian beam into double ring-shaped profile. This ring beam is most sharply defined at the focal image plane (FIP) which is the position of the image of the Gaussian beam waist formed by refraction in the slab of crystal. The FIP

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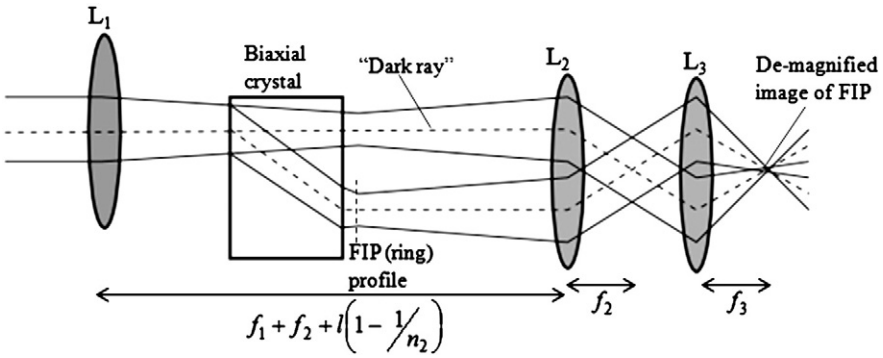


**Fig. 1.** The optical setup used to form a ring shaped beam at the focal plane of the objective $L_3$.

lies at a distance $f_1 + l(1-1/n_2)$ from lens $L_1$ where $l$ is the length of the crystal and $n_2$ is the intermediate principal refractive index. The crystal used was a 30 mm long slab of $KGd(WO_4)_2$ cut perpendicular to one of the optic axes. At the laser wavelength the principal refractive indices are: $n_1 = 2.01183$, $n_2 = 2.04235$, $n_3 = 2.09528$. The semi-angle $A$ of the light cone in the crystal is given by:

$$A = {}^{1}\!/_{n_2}\sqrt{(n_3-n_2)(n_2-n_1)} \tag{1}$$

and the radius of the light ring (the distance from the centre of the beam to the intensity minimum that separates the two rings) in the FIP is:

$$R_0 = Al. \tag{2}$$

Thus in our case $A = 0.019$ radians and $R_0 = 0.57$ mm. Fig. 2 shows a numerical simulation of the beam profile in the FIP, as described in Ref. [9]. The second converging lens $L_2$ ($f_2 = 20$ cm) was positioned such that the FIP lies at its back focal plane and a non-diverging Bessel beam is formed in the region of the focus on the other side of the lens. The is analogous to the formation of a zero order Bessel beam using an annular aperture located at the back focal plane of a converging lens, as described in Durnin et al. [5] except that our non-diverging beam is a superposition of zeroth and first order Bessel beams. In the non-diverging region the transverse intensity profile of the beam is:

$$I_{Non-Div}(r) \propto J_0^2(kr\ sin\theta) + J_1^2(kr\ sin\theta), \tag{3}$$

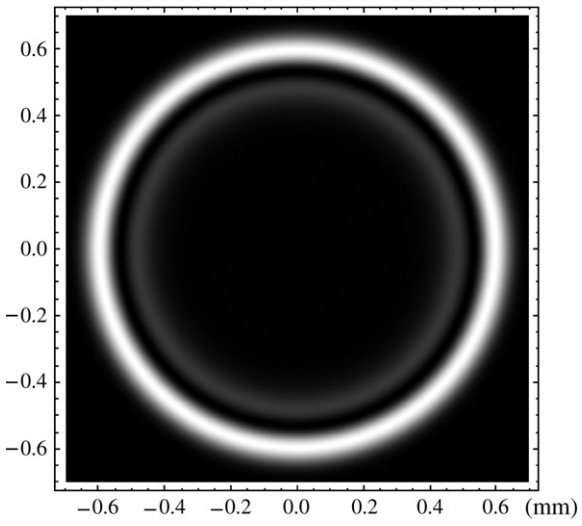


**Fig. 2.** A simulation of the beam profile at the back focal plane of $L_2$.

where $k$ is the wave number and $\theta$ is the semi-angle of the wave-vector cone. A 100x oil immersion microscope objective ($L_3$) was used to form a de-magnified image of the Bessel beam in a small sample of sol–gel resin placed on the underside of a 170 μm thick glass slide. This demagnified image of the Bessel beam is not quite non-diverging; rather it diverges with a semi-angle of 4°. The minimum radius of the central spot of the zeroth order beam is:

$$r_{spot} = {}^{1}\!/_{M}(2.405 / k\ sin\theta) \tag{4}$$

where $M$ is the magnification of the objective and

$$\theta = tan^{-1}\left({}^{R_0}\!/_{f_2}\right) \tag{5}$$

is the semi-angle of the conical superposition of wave-vectors produced by lens $L_2$. A demagnified image of the FIP is formed at the focus of the objective and the diameter, $d$, of that ring-shaped profile is:

$$d = 2R_0 \times {}^{f_3}\!/_{f_2} \tag{6}$$

which, for our setup, gives a value of 9.1 μm. The position of the glass slide (plus resin) in the x- and y-directions and the objective in the z-direction were controlled using computerised translation stages. The objective could be positioned so that either the ring-shaped beam or the Bessel-like beam lies near the glass-resin interface. Both of these positions were used for writing microstructures.

The preparation of the sol–gel resin has been described previously [4]. Essentially, a precursor containing 5 mol% Zr was prepared by hydrolysis of an organo-silane to which chelated zirconium alkoxide was added. Condensation reactions were promoted between the hydrolised precursors by the addition of water. The photo-initiator used was 4, 4′-bis(diethylamino) benzophenone (2% by weight) which has a high absorption cross-section at 400 nm. The sol–gel was allowed to dry on the glass substrate before mounting, inverted on the translation stage. The photopolymerisation process was monitored *in situ* using a CCD camera. The exposure time was varied using an optical shutter and was typically in the range of 10 ms to 1 s. The distance between the objective and the glass slide was also varied to explore the range of possible structures. Designating the position of the objective at which the ring profile is in focus on the glass–resin interface to be $z = 0$, structures were written at $z = 0$, 5, 10, 15 and 20 μm as the objective was moved away from the glass slide. Grid patterns with sub-micron thick walls were written by translating the sample in the x and y directions at constant speeds of 0.005 mm $s^{-1}$ in the Bessel region of the beam. After photopolymerisation the excess resin was washed away using isopropyl alcohol. A Zeiss He ion microscope and a Zeiss SEM were used to examine the polymerised microstructures.