Fabrication of woodpile structures by two-photon polymerization and investigation of their optical properties

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Abstract: Two-photon polymerization (2PP) is a powerful technique for the fabrication of 3D micro- and submicro-structures. By applying laser powers that are only slightly above the polymerization threshold, 3D structuring of photosensitive materials with a resolution down to 100 nm can be realized. Here we report on woodpile photonic crystal structures fabricated in organic-inorganic hybrid polymers (Ormocers) and investigation of their optical properties. The fabricated crystals possess a photonic band gap in the near infrared spectral region. The polymeric woodpile structures can be used as templates for the fabrication of highly refractive TiO_2 replicas. First results in this direction are presented.

OCIS codes: (140.7090, 160.5470, 220.4000)

References and links

1. S. Maruo, O. Nakamura, and S. Kawata, "Three-dimensional microfabrication with two-photon-absorbed photopolymerization," Opt.Lett. **22,** 132–134 (1997).
2. S. Kawata, H.-B. Sun, T. Tanaka, and K. Takada, "Finer features for functional microdevices," Nature (London) **412,** 697–698 (2001)
3. B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Rockel, M. Rumi, X.-L. Wu, S. R. Marder and J. W. Perry, "Two-photon polymerization initiators for three-dimensional optical data storage and microfabrication," Nature (London) **398,** 51–54 (1999)
4. H.-B. Sun, S. Matsuo, and H. Misawa, "Three-dimensional photonic crystal structures achieved with two-photon-absorption photopolymerization of resin," Appl. Phys. Lett. **74,** 786–788 (1999)
5. H.-B. Sun, V. Mizeikis, Y. Xu, S. Juodkazis,J.-Y. Ye, S. Matsuo, and H. Misawa, "Microcavities in polymeric photonic crystals," Appl. Phys. Lett. **79,** 1–3 (2001)
6. P. Galajda and P. Ormos, "Complex micromachines produced and driven by light," Appl. Phys. Lett. **78,** 249–252 (2001)
7. M. Deubel, G. von Freymann, M. Wegener, S. Pereira, K. Busch, and C.M. Soukoulis, "Direct laser writing of three-dimensional photonic-crystal templates for telecommunications," Nature Mat. **3**, 444-447 (2004)
8. M. Straub and M. Gu, "Near-infrared photonic crystals with higher-order bandgaps generated by two-photon photopolymerization," Opt.Lett. **27,** 1824–1826 (2001)
9. J. Serbin, A. Egbert, A. Ostendorf, B. N. Chichkov, R. Houbertz, G. Domann, J. Schulz, C. Cronauer, L. Fröhlich, and M. Popall, "Femtosecond laser-induced two-photon polymerization of inorganic-organic hybrid materials for applications in photonics," Opt.Lett. **28,** 301–303 (2003).
10. S.Y. Lin, J.G. Fleming, D.L. Hetherington, B.K. Smith, R. Biswas, K.M. Ho, M.M. Sigalas, W. Zubrzycki, S.R. Kurtz, and J. Bur, "A three-dimensional photonic crystal operating at infrared wavelengths," Nature (London) **394,** 251 (1998).
11. J.E.G.J. Wijnhoven, L. Bechger, and W.L. Vos, "Fabrication and characterization of large macroporous photonic crystals in titania," Chem.Mater. **13,** 4486–4499 (2001).

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1. Introduction

The research field of photonic crystals (PCs) is mainly driven by the theoretical modelling of propagation of light through periodic structures and by the development of more efficient numerical methods for the description of photonic crystal properties. The experimental realization of PCs with a complete, 3D bandgap in the visible or near infrared remains a major challenge that has not been solved so far. Photonic band-gap (PBG) materials must have a three dimensional periodicity with a period in the range of the light wavelength. Furthermore, the two distinct materials that form the periodic structure (generally a solid material and air) must have a contrast in refractive index of more than two. It has recently been demonstrated by several groups [1]-[8] that non-linear optical lithography based on two-photon polymerization (2PP) of photosensitive resins allows the fabrication of true 3D nanostructures and therefore, of 3D photonic crystals. When tightly focused into the volume of a photosensitive resin, the polymerization process can be initiated by non-linear absorption of near infrared femtosecond laser pulses within the focal volume. By moving the laser focus three-dimensionally through the resin, any 3D structure with a resolution down to 100 nm can be fabricated [9].

2. Experimental setup

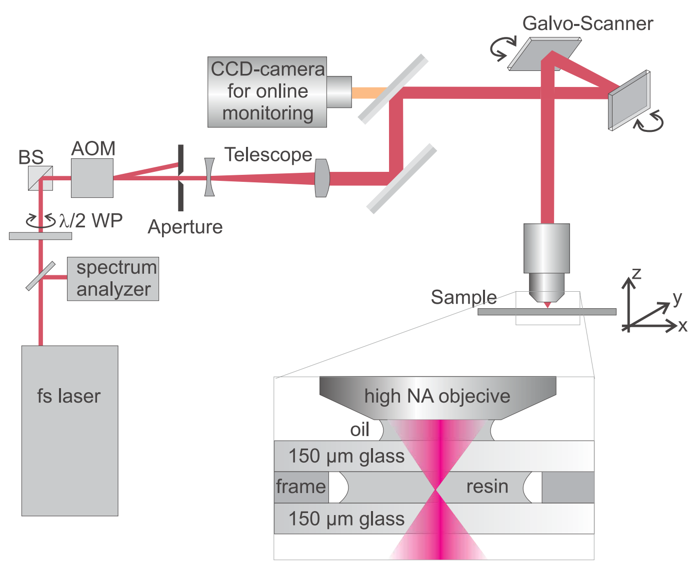

Fig. 1. Principle setup for the fabrication of 3D structures by 2PP. A waveplate (WP) together with a polarizing beamsplitter is used as an attenuator, an acousto-optical modulator (AOM) in combination with an aperture as a fast shutter. The beam is expanded by a telescope and then coupled into an x-y galvo scanner. The sample is mounted on a 3D piezo stage for positioning in all directions. A CCD camera placed behind a dichroic mirror is used for online monitoring of the 2PP process.

Figure 1 shows the principle setup that was used for the fabrication of 3D nanostructures by means of 2PP. Femtosecond laser pulses ($60\,fs$, $90\,MHz$, $< 450\,mW$, $780\,nm$) are tightly focused into the volume of a photosensitive resin with a high numerical aperture objective lens. Immersion oil was used for refractive index matching. For the positioning of the laser focus within the photosensitive resin, either a galvo scanner or a 3D piezo stage is applied. The CCD camera that is mounted behind a dichroic mirror is used for online monitoring of

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the 2PP process. Since the refractive index of the applied liquid polymer is slightly changed during polymerization, the illuminated structures become visible during the laser process as demonstrated in Fig. 2 and the respective movie. Here, the fabrication process of a micro-scale Venus statue is shown in real time.

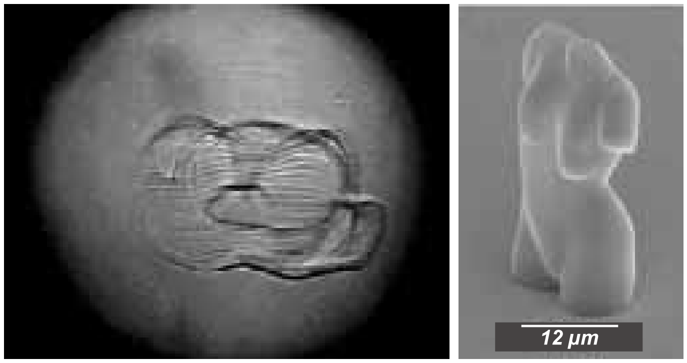

Fig. 2. Screenshot of a movie (2 MB) showing the fabrication process monitored online during two-photon polymerization of a -Venus statue (left, top view). SEM image of the respective Venus statue (right).

3. The applied polymers

Two different classes of materials have been applied for the fabrication of 3D nanostructures: Ormocers and SU-8. Both materials have been developed for optical applications and show high transparency in the visible and near infrared ranges. Ormocers are organic-inorganic hybrid polymers containing a highly crosslinkable organic network as well as inorganic components leading to high optical quality and mechanical as well as thermal stability. The polymerization process in Ormocers is initiated by radically reacting photo initiators (Igacure369 by Ciba). SU-8 on the other hand is an epoxy based resin with phenolic nuclei leading to their high transparency. Here, the crosslinking of the molecules is initialized by photoacid generators (PAGs). Under light exposure, the PAGs form strong acids which, by the application of heat, lead to irreversible crosslinking of the polymer. The steps needed for 2PP of both materials are summarized in table 1. The main differences of those two classes of materials are as follows: First, during exposure, Ormocers are in the liquid phase whereas SU-8 is solid. Second, Ormocers are thermally very stable whereas SU-8 can be removed by calcination in normal atmosphere at about 600°C. Third, online monitoring of the 2PP process is only possible in Ormocers since crosslinking in SU-8 does not occur before the application of heat (up to this moment there is no refractive index modification in SU-8).

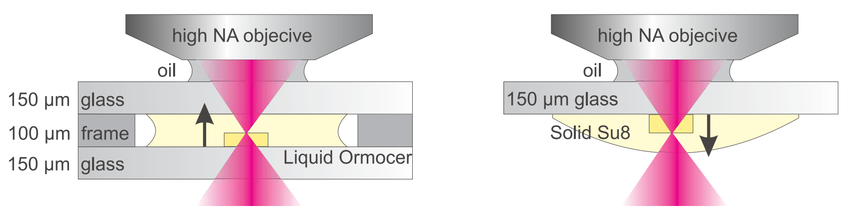

Fig. 3. Two different sample configurations are used, mainly determined by the phase of the polymer (liquid or solid)

The fact that Ormocers are liquid and SU-8 is solid also leads to different exposure strategies and sample configurations as they are shown in Fig. 3.

Procedure	Ormocer	SU-8
Softbake	1*min* at 80°*C*	50*min* at 95°*C*
Exposure	fs-pulses $p \simeq 45mW$	fs-pulses $p \simeq 20mW$
Postbake	no	12*min* at 95°*C*
Develop	30*s* in 4-methyl-2-pentanone	15*min* in *mr-Dev.-600*
Rinse	isopropanol	isopropanol
UV-curing	yes	no

Table 1. Steps needed for the fabrication of 3D microstructures by means of 2PP using Ormocer and SU-8 materials

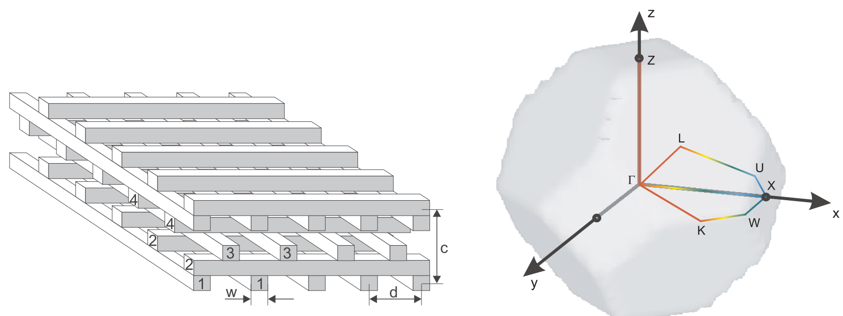

Fig. 4. Left: Sketch of a woodpile structure. w determines the width of the rods, d is the distance between the rods, and c is the height of a unit cell, containing four layers of rods. Right: Reciprocal lattice (first Brillouin zone) of the fcc woodpile structure. A path through the k-space containing points of high symmetry is indicated by the colored line.

4. Woodpile structures fabricated by means of 2PP

A sketch of a woodpile structure is shown in Fig. 4 (left). It consists of layers of one dimensional rods with a stacking sequence that repeats itself every four layers. The distance between four adjacent layers is denoted by c. Within each layer, the axes of the rods are parallel to each other with a distance d between them. The adjacent layers are rotated by 90°. Between every other layer, the rods are shifted relative to each other by $d/2$. Generally, the resulting structure has a face-centered-tetragonal (fct) lattice symmetry. For the special case of $c/d = \sqrt{2}$, the lattice can be derived from a face-centered-cubic (fcc) unit cell with the basis of two rods [10]. The unit cell of the reciprocal lattice is shown in Fig. 4 (right). The colored line indicates a path along high symmetry points through the k-space. The woodpile structure can also be derived from a diamond lattice by replacing the 110 chains of atoms with rods.

Figure 5 shows SEM images of different woodpile structures that have been fabricated by means of 2PP. The rods have a thickness of 300 nm and the in layer rod distance varies between $2\mu m$ (center) and 900 nm (right). The aspect ratio $c/d = \sqrt{2}$ has been kept constant resulting in an fcc symmetry of all crystals. Since the contrast in refractive index between the dielectric material (Ormocer) and air is of $n = 1.56$, the fabricated crystals do not possess a complete photonic bandgap (PBG). Nevertheless, in certain directions a PBG arises leading to a decrease in transmission. For optical characterization of the fabricated woodpile structures

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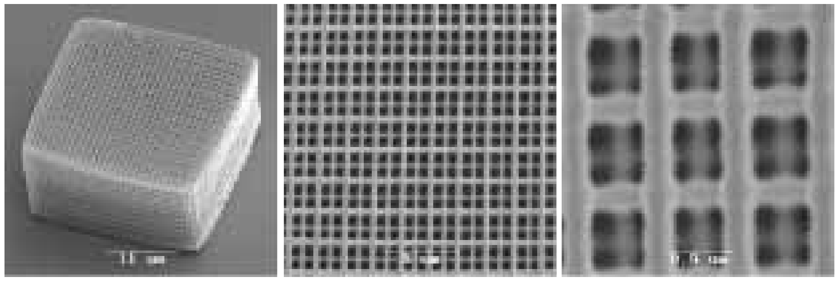

Fig. 5. SEM images of woodpile structures fabricated by means of 2PP in Ormocers.

Fouriertransform infrared spectroscopy (FTIR) was used. To provide necessary spatial resolution for the characterization of the photonic crystals with a total size of 60 μm, the spectrometer was coupled to an infrared microscope (with a 15$\times$ magnification).

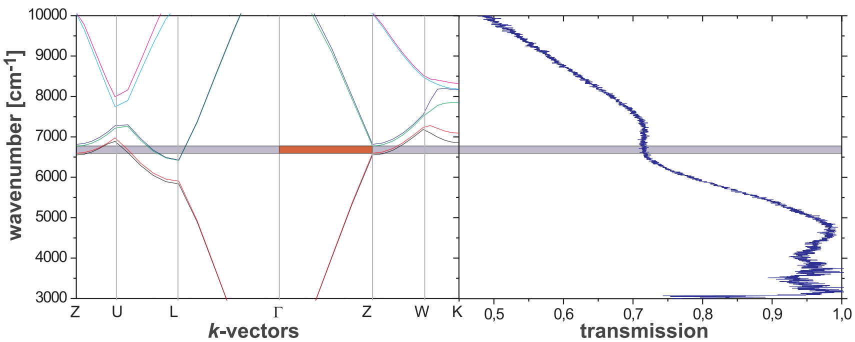

Fig. 6. Calculated band structure (left) of a polymeric woodpile crystal with an in layer rod distance of 1.2 μm and measured transmission (right).

The calculated band structure of a woodpile having an in layer rod distance of $d = 1.2\ \mu m$ is shown in Fig. 6, left. Calculations have been performed using a commercial ”Bandsolve” program and the plane wave expansion method. Due to the low contrast in refractive index the crystal does not possess a complete photonic band gap but there exists a band gap at 6700 cm^{-1} in the $(\Gamma - Z)$ direction (indicated by the red bar) which is the direction accessible by the IR-microscope. The transmittance of the respective woodpile structure fabricated by means of 2PP is shown in Fig. 6, right. At low wavenumbers (< 5000 cm^{-1}) the transmittance is close to unity. At the lower edge of the band gap the transmittance drops to a value of about 70%. Figure 7 (left) shows the measured transmission spectra for woodpile structures with different periods. The frequencies of the band gaps, located in the near infrared, scale with the period of the crystals according to the theoretical predictions. Theoretically, the transmittance should rise again to unity at frequencies above the band gap which was not observed in the experiments. The reason for that are disorder and imperfections within the fabricated crystal structures leading to wavelength dependent Rayleigh scattering scaling as λ^{-4}. To compensate the measured data for the losses due to Rayleigh scattering the transmission spectra shown in Fig. 7 (right) have been multiplied by a factor of

$$T = T_{measured} \left(1 - 0.4\lambda^{-4}\right)^{-1}, \qquad (1)$$

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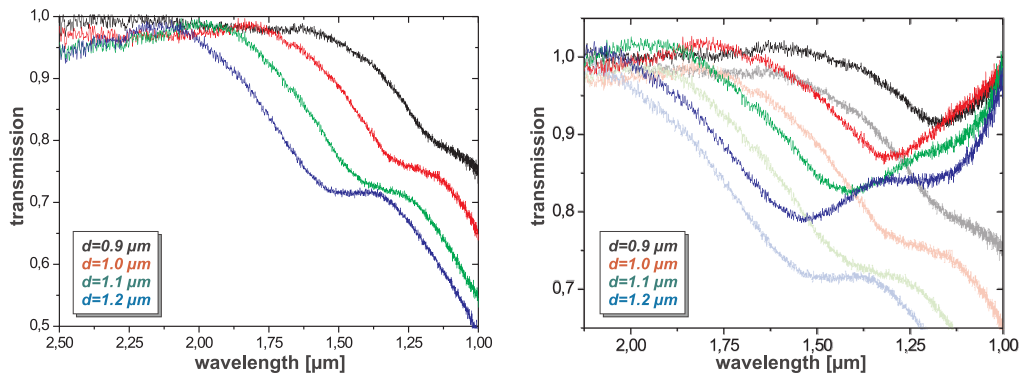

Fig. 7. Measured transmission of woodpile structures with different in layer rod distances.

where $T_{measured}$ is the experimentally derived transmittance, λ is the wavelength, and 0.4 is a fitting parameter obtained by setting the transmittance to unity at frequencies above the band gap. The problem with imperfections inside the fabricated photonic crystals is of purely technical nature. One needs better stability of laser and processing parameters than we have at present.

5. Infiltration

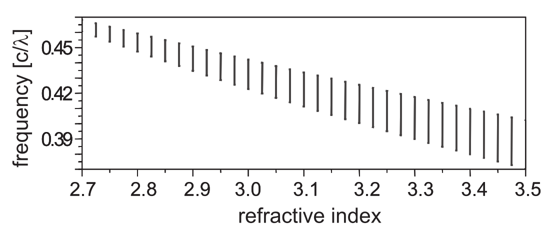

Fig. 8. Calculated gap map of woodpile structures as a function of the refractive index contrast.

Since the contrast in refractive index between air and the used polymers is too low to provide a complete PBG, woodpile structures fabricated in SU-8 by means of 2PP have been used as templates for the realization of highly refractive replica. Figure 8 shows the calculated gap map (i.e. the complete PBGs projected onto the vertical axis) for a varying contrast in refractive indices. The complete PBG arises at $n = 2.7$ and increases with increasing refractive index. Two possible, well established techniques have been considered for infiltration: Chemical vapor deposition (CVD) of silicon and infiltration with precursors forming nanoporous TiO_2, which is an established technique for the fabrication of inverted opal structures [11]. Since the temperatures needed for CVD exceed the tolerable temperature of SU-8, the infiltration technique was chosen.

First, the polymeric woodpile structures were fabricated by means of 2PP in SU-8 (see Fig. 9). Then, a single crystal was infiltrated with an excess of the precursor solution (80% titanium-IV-iospropoxide and 20% ethanol) for one hour in a helium atmosphere. After that, the infiltrated woodpile structure was exposed to the moisture in air for 12hours allowing the precursor to react with water to form solid, nanoporous TiO_2. In a subsequent calcination process, the polymeric template was removed by application of heat ($600^{\circ}C$ for 4 hours). Figure 10 (left)

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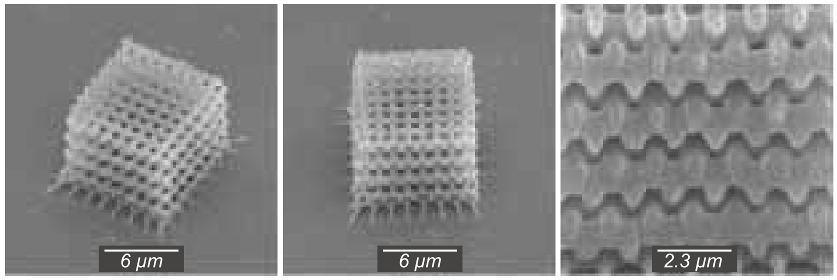

Fig. 9. SEM images SU-8 templates fabricated by means of 2PP.

shows an SEM image of a fragment of the inverted woodpile structure. The hexagonal arrangement of holes, which is indicated by the dashed line, can clearly be seen. To assure that the entire polymer had been removed during the calcination process, the structure was analyzed by means of energy dispersive x-ray analysis (EDX). The measured spectrum (Fig. 10, right) shows a peak at 2.2 keV that is caused by a gold layer on the sample which was needed to prevent the sample from charging in the electron beam. At 4.5 keV the titanium line appears. The carbon peak can hardly be seen indicating that almost all of the polymer was removed during the calcination process.

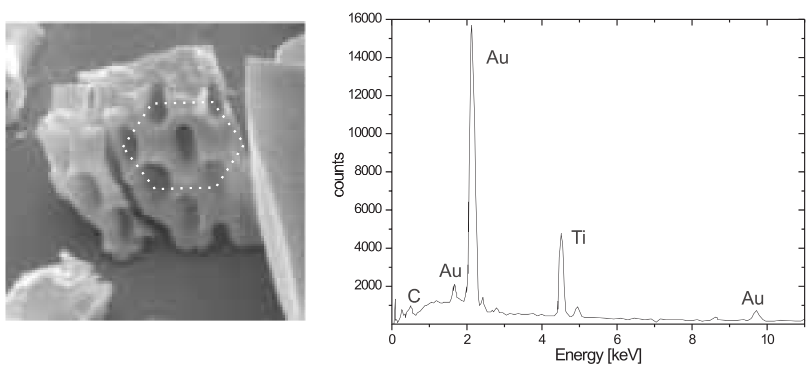

Fig. 10. SEM image of a fraction of an inverted woodpile structure and the respective EDX spectrum.

6. Summary

In conclusion, femtosecond laser induced 3D nanostructuring of of two different classes of polymers (Ormocers and SU-8), which both have excellent optical properties, have been performed. The fabricated Woodpile structures possess a photonic band gap in the near infrared spectral range. The central frequency of the band gap could be tuned by varying the crystal's period. Templates for the generation of inverted woodpile structures have been fabricated in SU-8 and their TiO_2 replicas have been produced.

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