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# 3D-structuring of optical waveguides with two photon polymerization

R. Inführ[1], J. Stampfl[1], S. Krivec[1] , R. Liska[1], H. Lichtenegger[1], V. Satzinger[2], V. Schmidt[2], N. Matsko[3], W. Grogger[3]

[1] TU Wien, Karlsplatz 13, 1040 Vienna, Austria
[2] Joanneum Research, Institute of Nanostructured Materials and Photonics, Franz Pichlerstr. 30, 8160 Weiz, Austria
[3] Institute for Electron Microscopy, TU Graz, Steyrergasse 17, 8010 Graz, Austria

## ABSTRACT

Two photon photopolymerization (2PP) is a new and modern method in solid freeform fabrication. 2PP allows the fabrication of sub-micron structures from a photopolymerizable resin. By the use of near-infrared (NIR) lasers it is possible to produce 3D structures with a spatial feature resolution as good as 200 nm. This technique can be used in polymer-based photonic and microelectromechanical systems (MEMS), for 3D optical data storage or for the inscription of optical waveguides based on a local refractive index change upon laser exposure. Since the 2PP only takes place inside the focus of the laser beam, complex 3D-structures can be inscribed into a suitable matrix material.

In the presented work, 2PP is used to write optical waveguides into a prefabricated mechanically flexible polydimethylsiloxane matrix. The waveguides were structured by selectively irradiating a polymer network, which was swollen by a monomer mixture. The monomer was polymerized by two photon photopolymerization and the uncured monomer was removed by evaporation at elevated temperatures. This treatment led to a local change in refractive index in the order of $\Delta n = 0.02$, which was significantly above the industrial requirement of $\Delta n = 0.003$. The measured optical losses were around 2.3dB/cm. Since all unreacted monomers were removed by evaporation, the final waveguide was stable up to temperatures of more than 200°C.

In a second approach highly porous sol-gel materials (based on tetramethoxysilane (TMOS) as precursor and the surfactant cetylpyridinium chloride monohydrate as structural template) were utilized as matrix materials. The precursor was organically modified with poly(ethylene glycol) spacers in order to increase the toughness and thus facilitate the fabrication of transparent porous monoliths and flexible films. The pores of the sol-gel-derived matrix were filled with acrylate-based monomers of high refractive index and after selective irradiation using 2PP waveguides ($\Delta n = 0.015$) could be written into the material.

## INTRODUCTION

Two photon polymerization (2PP) [1] [2]offers two distinct benefits over other solid freeform fabrication processes: (1) The achievable feature resolution is about one order of magnitude better than with other solid freeform fabrication (SFF) methods. The minimum achievable wall thickness is currently around 100nm [3]. (2) Furthermore it is possible to directly write inside a given volume. In contrast, all other additive SFF processes work by shaping individual 2D-layers and stacking up these layers in order to fabricate a 3D-model. Due to this additive stacking-process, it is not possible to embed existing components into a part made by traditional SFF processes. In contrast, 2PP is capable of writing “around” pre-embedded components. Despite these distinct advantages of 2PP, there are currently no commercial 2PP-applications, mainly due to the low writing speed of 2PP-systems and due to the complexity of the required lasers.

In Table 1 the speed of 2PP-lithography is compared with two commercial lithographic SFF processes (stereolithography – SLA; digital light processing – DLP) and injection molding as mass fabrication process. SLA is based on using a ultraviolet laser to selectively harden a photosensitive resin. Achievable feature resolutions are in the range of 5-10µm [4] and typical write speeds range from 100-1000mm/s. DLP is based on using a digital mirror device to project a two-dimensional bitmap onto a photosensitive resin. Thus a whole layer can be exposed in one shot, leading to high build speeds of about 20 vertical mm per hour [5].

To calculate the numbers listed in Table 1, a write speed of 10mm/s with a beam diameter of 20µm was assumed for 2PP. When considering the significantly higher equipment cost in combination with fairly low write speeds, it becomes obvious that the cost per written volume becomes prohibitively high in the case of 2PP.

*Table 1:* Speed comparison of different solid freeform fabrication techniques and injection molding.

| Process | Build speed | System cost | Machine cost | Machine cost |
|---|---|---|---|---|
| | $cm^3/hr$ | € | €/hr | €/$cm^3$ |
| SLA | 360 | 150 000 | 50 | 0,14 |
| DLP | 200 | 50 000 | 20 | 0,1 |
| 2PP | 0,014 | 300 000 | 100 | 7.142 |
| Injection molding | 480 | 50 000 | 20 | 0,04 |

In order to increase the productivity of 2PP, more efficient initiator systems [6] and more powerful laser systems have to be developed. Nevertheless, it cannot be assumed that 2PP will compete with other SFF methods or mass fabrication techniques (e.g. Injection molding) regarding throughput. Therefore 2PP is only interesting on an industrial level if the volume that has to be structured is fairly small. Considering these boundary conditions, an appealing application which makes use of 2PP's capability to write around pre-embedded components is the fabrication of optical waveguides for printed circuit boards (PCBs). For this application, only one dimensional lines have to be structured, which reduces the volume that has to be polymerized significantly.

**2PP-SYSTEM**

The laser system is a commercial ultrafast Ti:Sapphire laser (Spectra Physics), which comprises a Ti:Sapphire oscillator (Maitai) and a regenerative Ti:Sapphire amplifier (Spitfire), which is pumped by a frequency-doubled solid state Nd:YLF laser (Evolution X). The oscillator provides a pulse train at a repetition rate of 80 MHz and typical pulse duration of approx. 80 fs. Beam diameter is approx. 2 mm ($1/e^2$). The oscillator can tune its emission wavelength over the Ti:Sapphire emission spectrum from 750-850 nm. The oscillator pulse train seeds the regenerative amplifier, which boost the pulse energy up to 1mJ (1W average power), which is far beyond the required pulse energy for processing organic materials. The laser radiation properties change after amplification: the pulse duration is approx. 150 fs, the repetition rate is 1 kHz and the beam diameter increases to approx. 7 mm ($1/e^2$). The laser emission is synchronized to the sample motion by means of an electro-optical switch (on/off state) that additionally attenuates the laser power to a desired level (<300 µW) via remote control of the high voltage on the Pockels cell.

In order to improve the beam quality, the laser is fed through a spatial frequency filter to remove noise on the Gaussian TEM00 mode ($M^2$ factor of beam <1.05). The laser is focused in the sample by means of a 20x objective. Before entering the objective lens, the laser beam passes through a 1:3 cylindrical telescope, which introduces an elliptic beam shaping. This combination of optics is required for astigmatic beam focusing that yields a spherical focal volume instead of an ellipsoidal volume. The nearly spherical focal volume is an important prerequisite for waveguide writing because a spherical waveguide cross section is needed.

In order to control the depth of the laser focus relative to the sample surface, a depth profile is recorded prior to the laser writing. A collinear He-Ne laser is scanned through the sample (perpendicular to the sample surface) and the back reflected light is monitored in a confocal setup as a function of sample position. This way, a surface profile along the waveguide track can be recorded and used as reference for laser focus position, i.e. the laser focus is kept at a certain distance below the sample surface.

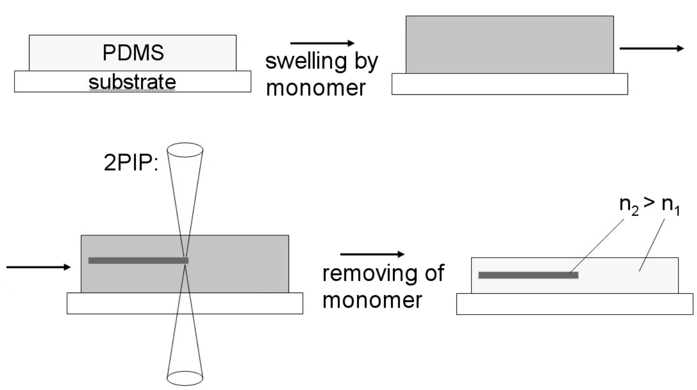



*Figure 1:* Principle of waveguide writing by 2PP into a PDMS matrix.

## MATERIALS

For this work two material classes have been investigated regarding their suitability for structuring waveguides for optoelectronic applications. Mechanically flexible waveguides have been written into a polydimethylsiloxane (PDMS) matrix [7], mechanically rigid waveguides could be structured using a sol-gel-based approach. After swelling a PDMS matrix with a suitable monomer formulation, the monomer was selectively photopolymerized by 2PP. Remaining uncured monomer was removed by evaporation at increased temperature and the final waveguides were obtained. Figure 1 illustrates this principle. As PDMS matrix the platin catalyzed thermally curing silicone rubber RT-601 was used.

For 2PP structuring 100 µm thick PDMS layers were swollen in monomer mixtures containing acrylic acid isobornyl ester (AIB), butandiol diacrylate BDA and 0.2 % 1,5-bis[4-N,N-dibutylamino)phenyl]penta-1,4-diyn-3-one (Bu-N-DPD) for several hours and afterwards exposed with above described 2PP-setup. The focus of the 800 nm femtosecond laser was scanned across the material volume, which left an embedded structure in the PMDS matrix.

AIB swells PDMS very well and led to polymer contents in the range of 50 %. In order to control the degree of swelling and the according polymer content, decanol was used as a co-solvent. Due to its polar properties it swells PDMS only little. By using different monomer mixtures of AIB and decanol the swelling of PDMS was controlled. In Figure 2 (left) the achieved refractive index change in dependence of the polymer content is depicted. At medium polymer contents, Δn is approximately 0.02, which is well above the required limit.

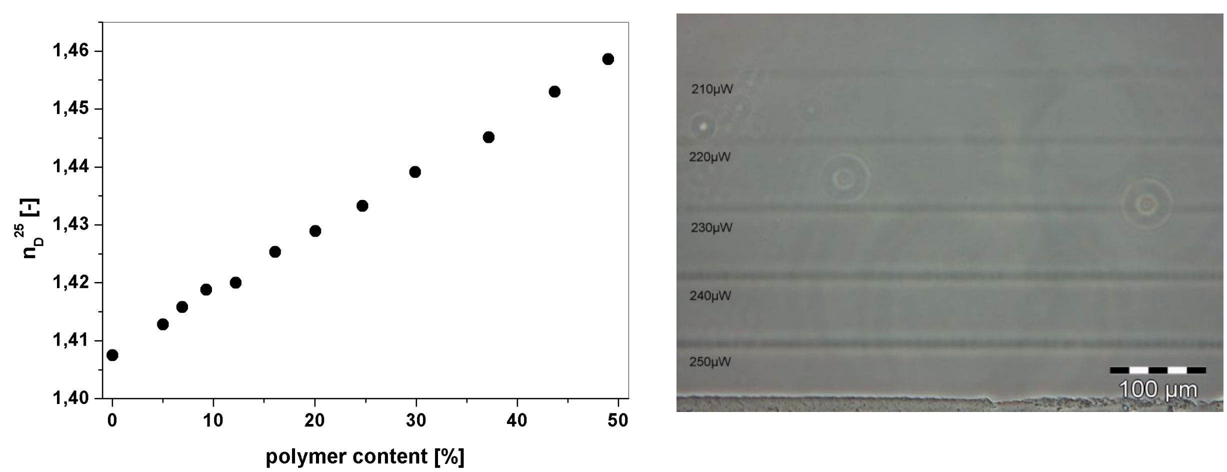



*Figure 2:* Refractive index change in dependence of polymer content (left). Waveguides written by 2PP as seem by phase contrast microscopy (right).

## Sol-gel based waveguide materials

Based on the idea of true liquid crystal templating, porous carrier materials based on the sol-gel chemistry were developed. Pores should be able to get infiltrated by a monomer that can be photopolymerized in a subsequent step by 2PP. Residual monomer in the cladding material can be evaporated to ensure lower refractive index (Figure 3).

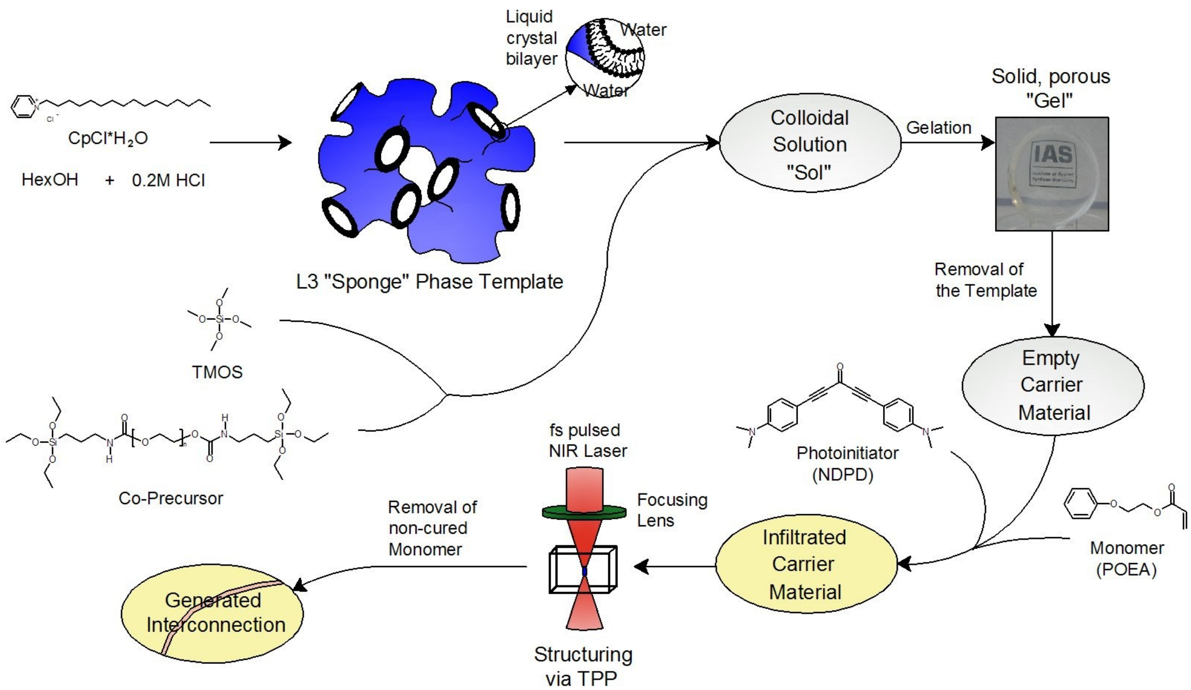



*Figure 3:* Pathway to fabricate optical interconnection as waveguides by 2PP in a porous silica carrier material.

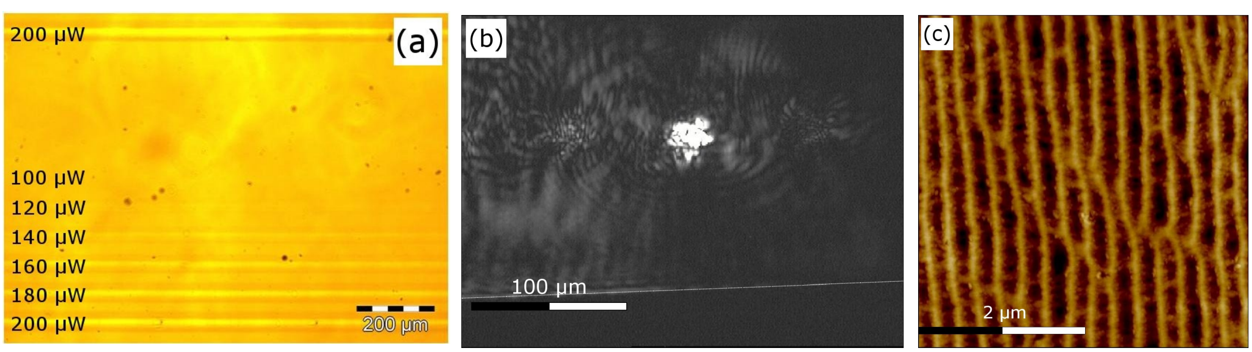
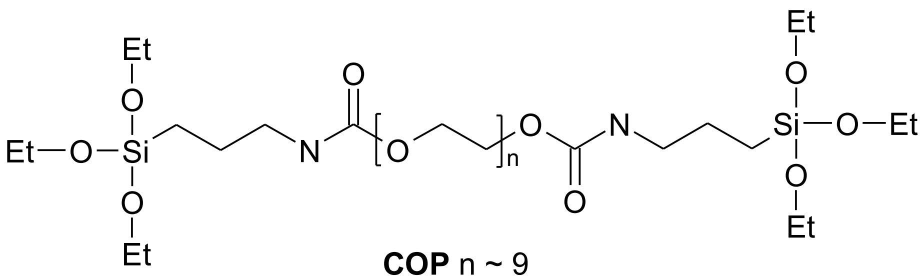
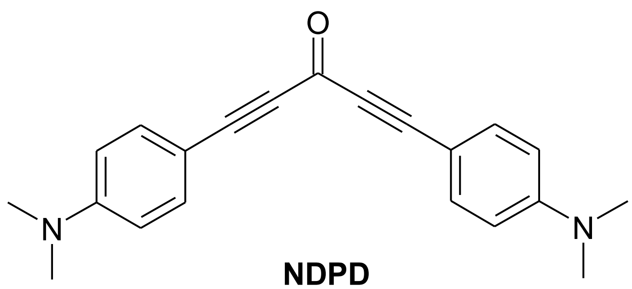



*Figure 4:* (a) Light microscopy images showing POEA waveguide bundles with a spacing of 75 µm structured in a monolithic sample D3 with different laser power. (b) Light outcoupling from waveguides structured with 100 µW. (c) AFM height image.

As such sol gel based hybrid materials from tetramethoxy silane (TMOS) suffer from high brittleness, a hybrid coprecursor COP (Figure 5) based on the addition reaction of polyethylene glycol 400 and isocyanatopropyl triethoxysilan was synthesized following a procedure described by Kricheldorf et. al.[8]. Monoliths and thin films were obtained following the procedure described by McGrath et.al [9] , with the exception of using the organically modified co-precursor in relative amounts of 5, 10 and 20 wt%  in addition to TMOS. By this method we were able to fabricate crack free monoliths and flexible films.



**COP** n ~ 9



**NDPD**

*Figure 5: Co-Precursor COP and TPA photoinitiator NDPD.*

The mechanical properties were investigated in terms of indentation modulus and indentation hardness, respectively. When stored in solvent, the enhanced material remained accessible for monomer infiltration (Phenoxyethylacrylate with 0.2 wt% NDPD [6]as photoinitiator ). Thus waveguides could be successfully structured by applying the two photon polymerization technique (Figure 4a). Refractive index changes up to $\Delta n = 0.015$ could be achieved. Furthermore, their ability to guide light could be shown (Figure 4b). However, the addition of co-precursor caused a shift of the template from the “sponge” like $L_3$ phase into the adjacent $L_\alpha + L_3$ blend caused by thermodynamic reasons. Atomic force microscopy gave a proper insight into this transition (Figure 4c).

## CONCLUSIONS

Using PDMS and sol-gel-derived siloxanes as matrix material waveguides coud be written successfully using 2PP. By infiltrating the porous matrix with photosensitive resins, a refractive index change between $\Delta n = 0.015$ (sol-gel-approach) and $\Delta n = 0.02$ (PDMS) could be achieved. The currently possible write speeds of 2PP (0.5-10mm/sec) favor applications where only small volumes have to be polymerized. Due to the one-dimensional character of waveguides this application is highly suitable for 2PP. A further benefit is 2PPs capability to incorporate existing components (e.g. laser- and photo-diodes) into the build volume.

## ACKNOWLEDGMENTS

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