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Materials for the fabrication of optical waveguides with two photon photopolymerization

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Abstract

Two photon photopolymerization (2PP) is an innovative method for 3D-structuring structural and functional materials. 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 micro-electromechanical systems (MEMS), for 3D optical data storage or for the inscription of optical waveguides into materials 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.

Since commercially available one-photon-photoinitiators are only of limited use for 2PP, a new class of photoinitiators (PIs) has been developed. These PIs exhibit a large 2PP-crossection and therefore contribute to a process with higher throughput. The PIs were evaluated using UV-Vis and fluorescence measurements. The TPA-cross-section was determined by the use an open aperture Z-scan technique. In 2PP structuring tests the ideal building parameters for each PI were determined, indicating that the presented PIs can be used at very low concentrations (0.05 wt%).
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2 Introduction

Two photon polymerization (2PP) [1] [2] offers two distinct benefits over other additive manufacturing processes: (1) The achievable feature resolution is about one order of magnitude better than with other additive manufacturing technologies (AMT). 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 AMT 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 AMT. 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. 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.

3 2PP system

Two different 2PP setups (system 1 is based on an amplified femtosecond laser, system 2 utilizes no amplifier) were used for structuring the parts shown in this paper.

2.2 Amplified 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.

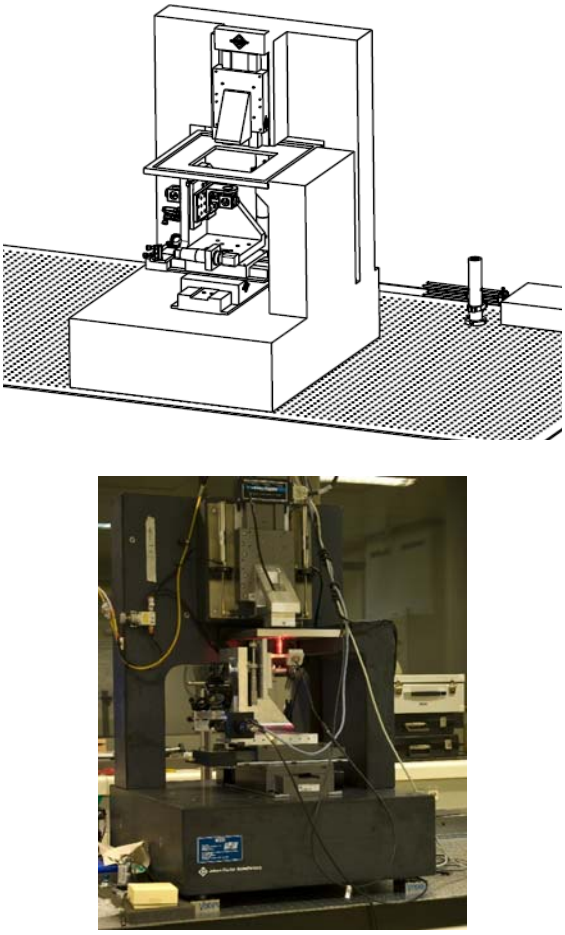

Fig. 1: *M3DL structuring device – schematic drawing (top) and setup of the system (bottom)*

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.

2.3 Non-amplified system

The second system (M3DL) uses an ultrafast Ti:Sapphire laser (High-Q Laser), having a repetition rate of 73 MHz and a pulse width of less than 100 fs. The beam diameter after the laser head is approx. 2 mm. The average laser power at 810 nm is 225 mW.

The laser beam passes through a collimator positioned after the laser head. As an electro-optical switch an Acousto-optic modulator (AOM) is being used.
The structuring device (M3DL) was developed by LZH (Laser Zentrum Hannover) [4] specifically for writing large 2PP-structures at high writing speeds.
The structuring unit (Fig. 1) is based on a x - y scanner which consists of two linear air-bearing stages. These two stages carry the complete optical setup including a CCD-Camera for live imaging and the microscope objective. The air bearing stages have a positioning accuracy of 20nm and facilitate high structuring speeds up to 20 mm/s.
The main benefit by using a xy-Scanner instead of a Galvanoscanner is that the objective focal point remains in plain for the hole structuring area (40x40 mm). For structuring waveguides by using the 2PP process a long and accurate focus travel path is necessary.

4 Materials

A 100 µm thick layer (matrix material) of a platin catalyzed thermally curing silicone (Elastosil RT-601) was swollen in a monomer mixture 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 (B3K) for several hours and afterwards exposed with above described 2PP-setup. The monomer contained a diionone based two-photon initiator [5, 6] to trigger the photopolymerization upon irradiation. The focus of the 800 nm femtosecond laser was scanned across the material volume, which left an polymerized structure in the PDMS matrix. The uncured monomer was removed by evaporation.
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 (top) 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.
For structuring the waveguide into the swollen PDMS the focus of the femtosecond laser was moved across the volume of the matrix material. After the scanning process an embedded waveguide is left in the matrix (Fig. 2, bottom).

5 Results

Using the amplified system, waveguides with a scanning speed of 20mm/min could be written. The achieved refractive index change was around $\Delta n = 0.02$. Using a non-amplified laser, significantly higher write speeds around 100mm/min could be achieved. Test structures fabricated with the M3DL-system are depicted in Fig. 3. The bottom image in Fig. 3 represents an online-observation of the writing-process during the fabrication of a waveguide.

6 Conclusion

Using PDMS as matrix material waveguides could be written successfully using 2PP. By infiltrating the porous matrix with photosensitive resins, a refractive index change of $\Delta n = 0.02$ could be achieved. The currently possible write speeds of 2PP (5-100mm/min) favour 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.

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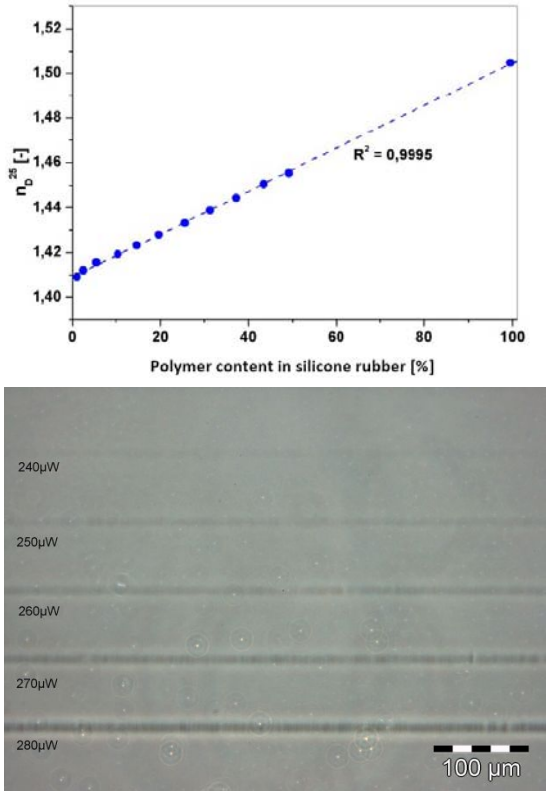

Fig. 2: *Achieved refractive index change (top) in dependence of monomer content in the matrix. The lower picture depicts waveguides written into PDMS using varying laser powers.*

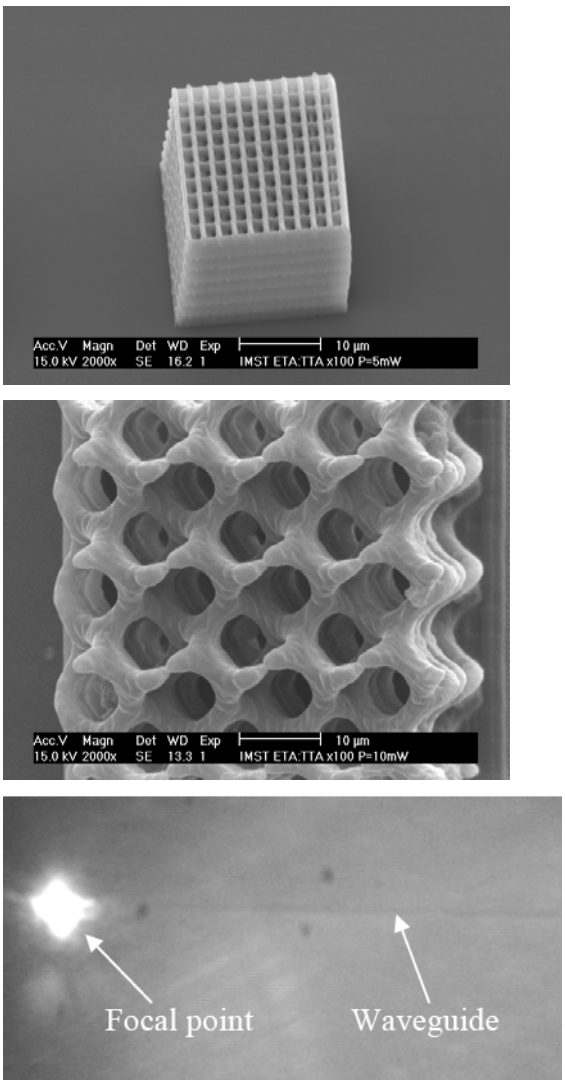

Fig. 3: *Test structures (top and middle) fabricated using a non-amplified laser system. The bottom image shows a life image of the write process. The bright point represents the laser focus, the dark line the polymerized waveguide. .*