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REFRACTIVE INDEX PATTERNING OF FLEXIBLE WAVEGUIDE MATERIALS BY MEANS OF TWO-PHOTON 3D LITHOGRAPHY

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1 Introduction

Two-photon induced photopolymerization (2PIP) is a new and modern field in solid freeform fabrication [1]. 2PIP allows the fabrication of sub-micron structures from a photopolymerizable resin. By the use of near-infrared lasers it is possible to produce 3D structures with a spatial fabrication resolution down to 120 nm [2].

This technique can be used e.g. in polymer-based photonic and microelectromechanical systems, for 3D optical data storage or to inscribe waveguides into materials that are otherwise not accessible. Since the 2PIP only takes place inside the focus of the laser beam, complex 3D structures (e.g. waveguides) can be inscribed into a matrix material to carry out such difficult tasks as connecting two optical components already embedded in a 3D block of transparent material.

Polydimethylsiloxane (PDMS) is a suitable matrix material because it is mechanically flexible, cost effective, temperature-resistant up to 290 °C and has low optical attenuation (lower than 0.02 dB/cm at 850 nm) [3]. Waveguides made from polysiloxanes are usually fabricated from thermosetting siloxanes by lithographic methods combined with reactive ion etching or by using molds [4].

For practical waveguide applications the 2PIP has to induce a refractive index change in the order of $\Delta n/n \sim 0.1\,\% - 1\,\%$. [1]

In this paper we report successful 3D structuring of optical waveguides in a preformed PDMS matrix by 2PIP. After swelling a PDMS matrix, the monomer was selectively photopolymerized by 2PIP. Remaining monomer was removed by evaporation at increased temperature and the final waveguides were obtained. Figure 1 illustrates this principle.

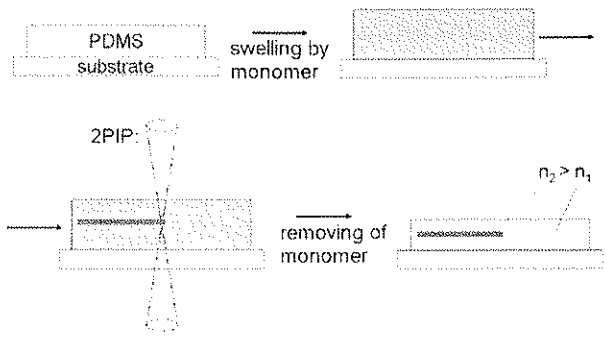


Figure 1: Principle of waveguide writing by 2PIP into a PDMS matrix

2 Experimental

2.1 Materials and characterization

Chemicals were purchased from Sigma-Aldrich unless otherwise noted and were used without further purification. For preparing PDMS specimens the two component silicone rubber Elastosil RT-601 (from Wacker) was used because it already applied in waveguide applications [3]. Fourier-transformed infrared measurements were performed on a Bruker "Tensor27" with a "DuraSampl IR II" ATR attachment. Refractive indices of PDMS specimens were measured by an Abbe refractometer at 590 nm and 25 °C. As a light source for photopolymerization a mercury UV lamp was used. TGA measurements were performed on a TGA 2050 (TA Instruments) under air at a heating rate of 10 °C/min.

2.2 Preparation of PDMS specimens

As PDMS matrix the platin catalyzed thermally cured silicone rubber RT-601 was used. The pot time of this composition was more than 60 min, which was sufficient for handling. PDMS discs with a diameter of 8.0 mm and a thickness of 2.0 mm were cured for 20 h in a mold at 75 °C.

The PDMS discs were swollen for 20 h at room temperature in the particular monomer mixture containing 1.0 % of 2-hydroxy-2-methyl-1-phenyl-1-propanone (from Ciba) as photoinitiator. Acrylic acid isobornyl ester (AIB) was used as monomer. Decanol (DEC) was used as an inert co-solvent to reduce swelling and control the polymer content of cured PDMS discs. Butandiol diacrylate (BDA) acted as a co-monomer for reducing swelling. Via the increase of weight after swelling, the monomer content of silicone discs was calculated.

Swollen specimens were cured under argon by an UV lamp for 10 min and were heated to 75 °C for 20 h to remove unreacted monomer. The monomers could also be removed more gently under reduced pressure. Some non-crosslinked compounds were washed away from the PDMS matrix during swelling. The specific amount was dependent on the monomer mixture and was determined from the weight loss of the pristine PDMS after swelling and removing of the monomer at 75 °C. This systematic error in the range of 0.5 - 2.0 % was corrected.

Monomers were examined regarding their swelling properties of the PDMS matrix and their behavior during photopolymerization.

2.3 Two-photon induced photopolymerization (2PIP)

For 2PIP 100 µm thick PDMS layers (Elastosil RT-601) were swollen in monomer mixtures containing AIB, 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 exposed to the laser. The focus of the 800 nm femto-second laser was scanned across the material volume, which left an embedded structure in the PMDS matrix. The detailed procedure is described elsewhere [5].

3 Results and discussion

3.1 Control of resulting polymer content of PDMS

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, DEC was used as a co-solvent. Due to its polar properties it swells PDMS only little. By using different monomer mixtures of AIB and DEC the swelling of PDMS was controlled. Figure 2 shows the monomer mixture content after swelling and the resulting poly-AIB content of PDMS specimens after irradiation by UV-light and removing of unreacted volatile compounds at elevated temperature.

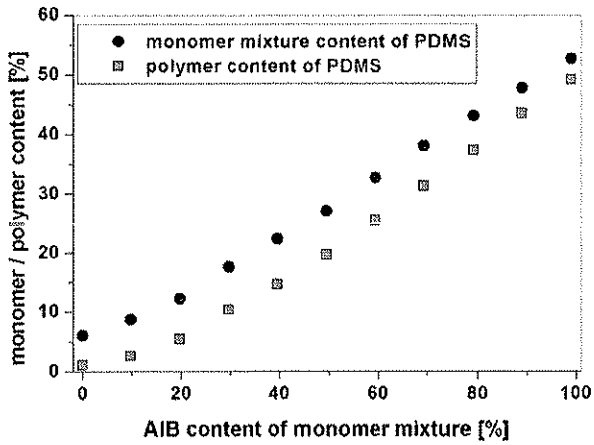


Figure 2: Swelling properties of PDMS in mixtures with AIB and DEC

Another approach for controlling the swelling properties of monomer mixtures was the use of BDA as co-monomer. BDA swells PDMS little (see figure 3) and is able to increase the thermal stability of the formed polymer-PDMS networks due to its crosslinking properties.

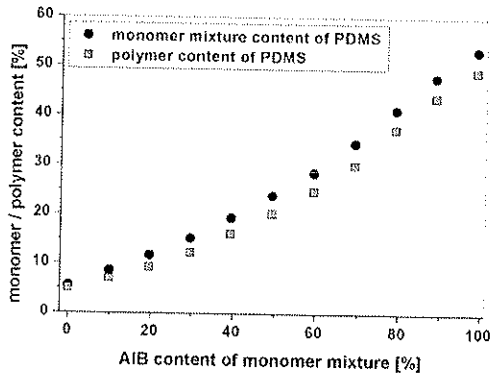


Figure 3: Swelling properties of PDMS in mixtures with AIB and BDA

3.2 Monitoring the polymer content of PDMS by ATR-IR-spectroscopy

In addition to the weighing procedures used above to quantify the amount of additional matter in the swollen PDMS samples, ATR-IR-spectroscopy was applied to unambiguously identify the polyacrylate component within the PDMS matrix. IR spectra of pristine PDMS samples were measured as reference. The polyacrylates exhibited a band around 1725 cm^{-1} due to the stretching vibration of the C=O bond (see figure 4).

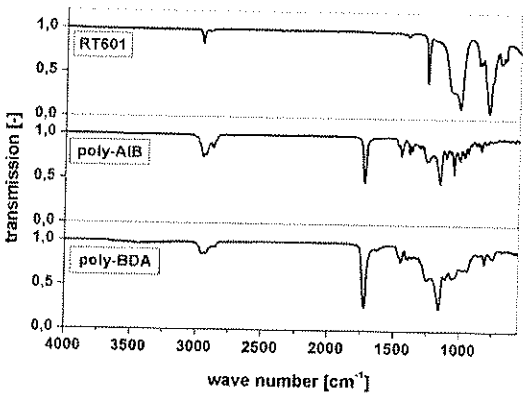


Figure 4: ATR-IR-spectra of RT-601, poy-AIB and poly-BDA

By integrating the C=O-bands of PDMS samples containing increasing amounts of poly-AIB, a linear relation between the peak area and the poly-AIB content exhibited (see figure 5). PDMS samples, which only contained poly-AIB, were derived by swelling in mixtures with AIB and DEC.

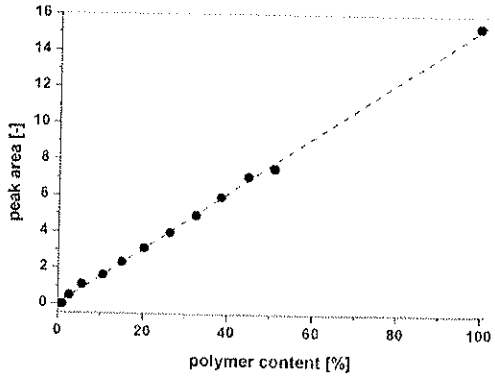


Figure 5: Correlation between C=O-band peak areas and poly-AIB content of PDMS samples

PDMS samples containing co-polymers of AIB and BDA showed no linear correlation between polymer content and corresponding peak area (see figure 6). The data at polymer contents of 99 % (figures 5 and 6) correspond to the homopolymers of AIB and BDA containing 1.0 % of photoinitiator.

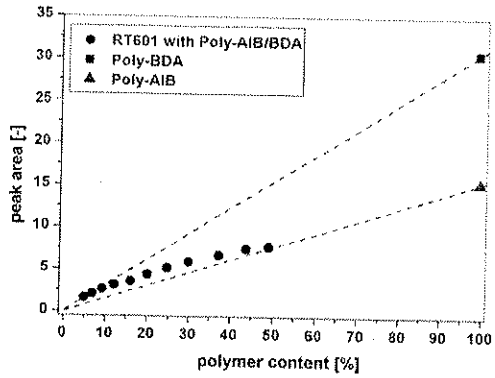
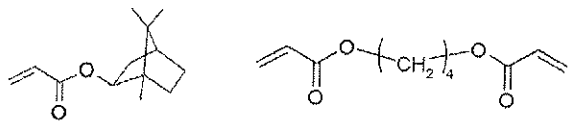


Figure 6: Correlation between C=O-band peak areas and poy-AIB/BDA content of PDMS samples

The reason for the non-linear characteristic in figure 6 was that BDA contains two C=O-groups at a very similar molecular weight (M_w) compared to AIB. At the lowest polymer content of the PDMS (5 % poly-BDA) the peak area of the IR-spectra shows a tendency to the homopolymer of BDA, while at the highest polymer content of the PDMS (49 % poly-AIB) there is a tendency to the homopolymer of AIB. Figure 7 shows the molecular structures of AIB and BDA.



AIB (M_w = 208 g/mol) BDA (M_w = 198 g/mol)

Figure 7: Chemical structures of AIB and BDA

3.3 Influence of the polymer content of PDMS on the refractive index

The refractive index of cured PDMS specimens containing only poly-AIB showed a linear correlation between polymer content and refractive index. (see figure 8)

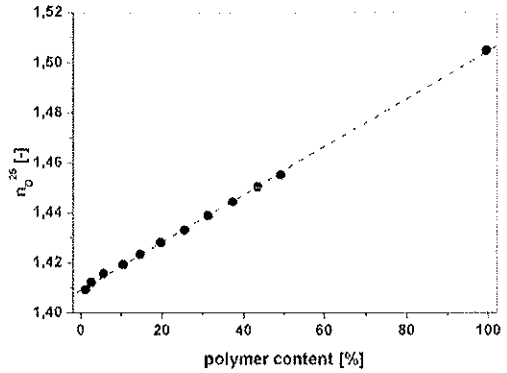


Figure 8: Refractive index of PDMS with poly-AIB

PDMS specimen, which contained co-polymers of AIB and BDA, also showed a virtually linear correlation between polymer content and refractive index (see figure 9). That makes it possible to control the refractive index change of irradiated PDMS areas easily by adjusting the swelling properties of a monomer mixture consisting of AIB and BDA.

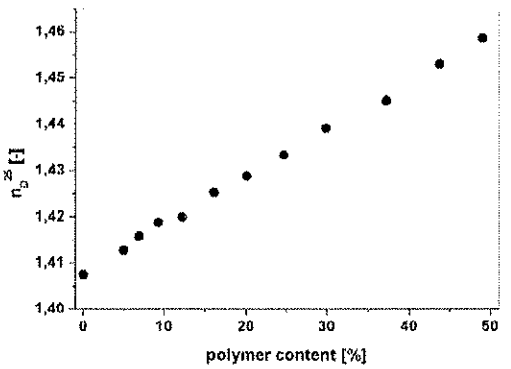


Figure 9: Refractive index of PDMS with poly-AIB/BDA

3.4 Increasing the thermal stability with BDA as crosslinker

An increased thermal stability is important for the potential use in circuit board applications, where short-term temperatures above 250 °C may occur. When BDA is used as co-monomer it acts as a crosslinker and increases the thermal stability of the resulting co-polymer inside the PDMS matrix [6]. For better comparison the decomposition temperature of a polymer can be considered as the temperature at that 5 % weight loss occurs [7]. Figure 10 shows the TGA-curves of the homopolymers poly-AIB and poly-BDA. Poly-AIB is a linear polymer and decomposed at around 269 °C while the highly crosslinked poly-BDA decomposed at around 367 °C (see table 1).

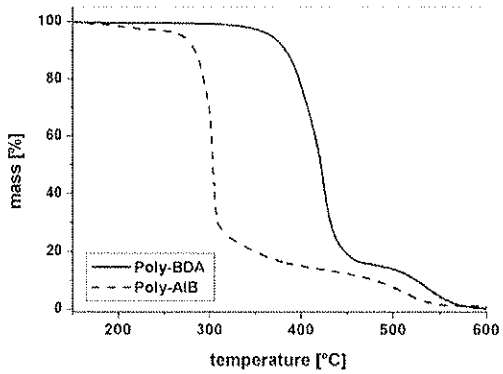


Figure 10: TGA-curves of poly-AIB and poly-BDA

Figure 11 compares the TGA-curves of the pristine PDMS with PDMS specimens that contained the homopolymers of AIB and BDA and varying amounts of the co-polymers of AIB/BDA. Due to the differing polymer contents of the PDMS samples a direct comparison of the decomposition temperatures was not reasonable. Nevertheless a general tendency of increased thermal stability of crosslinked samples was observed (see table 1).

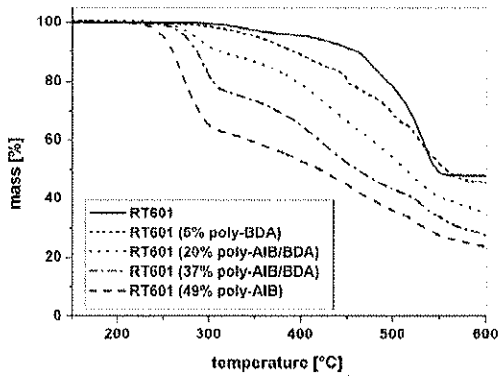


Figure 11: TGA-curves of PDMS containing different amounts of polymer

Table 1: Results of TGA-measurements

sample description	monomer mixture [AIB/BDA]	temp. at 5% weight lost [°C]
poly-AIB		269
poly-BDA		367
RT-601 (pristine)		409
RT-601 (5 % poly-BDA)	0/100	353
RT-601 (20 % polymer)	50/50	284
RT-601 (37 % polymer)	80/20	275
RT-601 (49 % poly-AIB)	100/0	250

3.5 Waveguide writing by 2PIP

Figure 12 shows the chemical structure of the recently developed photoinitiator 1,5-bis[4-N,N-dibutylamino)-phenyl]penta-1,4-diyn-3-one (Bu-N-DPD), that was

derived from 1,5-bis(4-(dimethylamino)-phenyl)penta-1,4-diyn-3-on (N-DPD), a highly reactive photoinitiator for 2PIP [8]. With its more apolar chemical structure Bu-N-DPD showed an increased compatibility with the PDMS matrix, resulting in a high phase contrast of the resulting waveguides, which indicated a sufficient waveguide performance. Best results were obtained using a monomer mixture containing 60 % AIB, 40 % BDA and 0.2 % Bu-N-DPD. The feedrate of the laser for 2PIP was 10 mm/min.

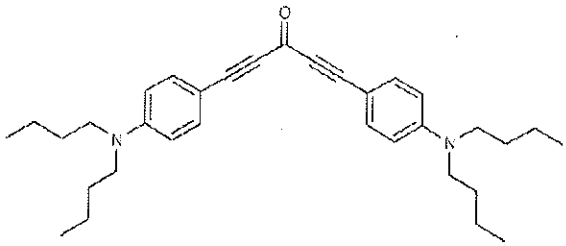


Figure 12: Chemical structure of Bu-N-DPD

It was found that the processing window and therefore the range of laser power between high phase contrast and the destruction of the material was approximately 30 µW (see figure 13).

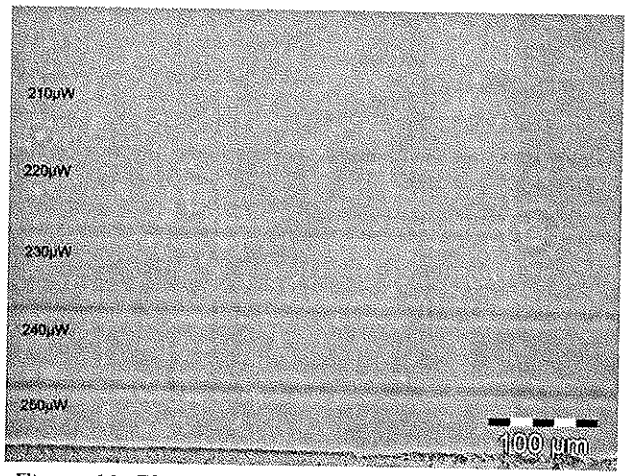


Figure 13: Phase contrast microscopy image of optical waveguides structured by 2PIP

The single waveguides had diameters between 10 - 15 µm (see figure 13). By writing a waveguide bundle of 11 waveguides a homogeneous optical waveguide with a diameter of 40 µm was obtained. The location of the waveguides is indicated by the bright spots (see figure 14), because the waveguide transmits the light from the microscope illumination better than the surrounding material. This is only a qualitative visualization of the waveguide, because the visibility is strongly depending on the illumination conditions [9].

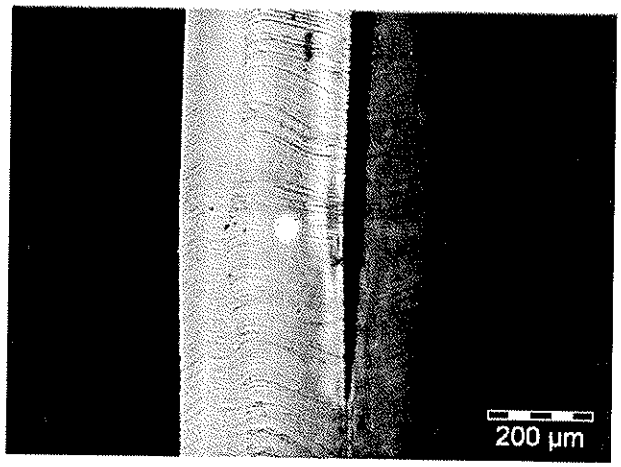


Figure 14: Cross-section of a waveguide bundle

Presuming complete photopolymerization during 2PIP the polymer content of the obtained waveguides was around 25 %, according to a refractive index increase of $\Delta n = +0.026$ ($\Delta n/n = 1.8$ %).

4 Conclusion

PDMS was tested as a mechanically flexible matrix for optical waveguides that were structured by 2PIP. A flexible PDMS matrix was swollen by a monomer mixture, which was selectively photopolymerized by 2PIP to increase the refractive index in the exposed area. Afterwards the uncured remaining monomer was removed at increased temperature. The degree of swelling of the PDMS matrix was controlled by the monomer formulation containing a mixture of AIB, BDA and the recently developed two-photon active photoinitiator Bu-N-DPD. BDA reduced swelling and increased the thermal stability of the obtained PDMS-polyacrylate hybrid material. The achievable change of refractive index using this method is in the range of $\Delta n = +0.030$ ($\Delta n/n = 2.1$ %).

5 Acknowledgements

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6 References

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