Two-Photon Polymerization of hybrid polymers for applications in micro-optics

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ABSTRACT

Miniaturization and higher integration of opto-electronic components require highly sophisticated optical designs. This creates the demand for freeform technologies like Two-Photon Polymerization (2PP) and new specially adapted materials like hybrid polymers (ORMOCER®s). Recent progress in the fabrication of microoptical structures using 2PP and specially designed hybrid polymers is presented. Among the structures are freeform and aberration-optimized microlenses and multilevel diffractive optical elements. These components are discussed with respect to fabrication process and their resulting optical performance. Furthermore, 2PP-initiated refractive index modification, offering high potential for energy-efficient fabrication of 3D optical interconnects, is discussed.

Keywords: two-photon polymerization, two-photon absorption, hybrid polymers, diffractive optical elements, microoptics, optical interconnects, waveguides

1. INTRODUCTION

Microoptical elements play a major role in the miniaturization and integration of opto-electronic devices. Examples are light trapping structures for efficient photovoltaics or novel multi-aperture camera systems. However, classical fabrication technologies, such as, e-beam lithography, focused ion beam milling, selective chemical etching, photore sist reflow, and gray-tone lithography are limited to few standard geometries. On the other hand, microoptical elements with freeform surfaces can further improve device performance and open the way to new optical functionalities. Two-photon polymerization (2PP) is a rapid additive manufacturing technology being inherently capable of fabricating arbitrary microstructures in photopolymers, comparable to 3D printing, however, with much higher precision of the final structures. Its freeform capability is enabled by employing focused femtosecond laser pulses in order to confine the solidification of the photopolymer to the tiny focal volume. Scanning this volume in 3D space allows to fabricate arbitrary structures from, e.g., CAD design files or other sources of 3D data. Consequently, 2PP has been used in a variety of applications in microoptics (lenses, fibers, waveguides, biomedicine (scaffolds, drug delivery, valves) and other fields of research (metamaterials, micromechanics)). By means of three examples, microlenses, diffractive optical elements (DOEs), and refractive index patterning, the advantages of 2PP for the fabrication of microoptical structures are demonstrated.

2. MATERIALS AND METHODS

For the 2PP fabrication, a custom-built 3D fabrication system is employed, consisting of a light source, a fast shutter for computer-controlled light switching, and a 3D positioning system. To trigger two-photon absorption (TPA) and thus to initiate two-photon polymerization, a frequency doubled Ytterbium-doped femtosecond oscillator (Amplitude Systems t-pulse 200), which emits 1030/515 nm, 350 fs pulses at a repetition rate of 10 MHz is used.

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used. Synchronizing the lasers on/off state with the position of the focal volume in the sample is accomplished by employing an acousto-optical modulator (AOM, Amplitude Systems) in combination with the PSO (position synchronized output) feature of the controller of the positioning system (Aerotech NPaq/A3200). This enables position-synchronized laser switching on the time-scale of microseconds. The desired pulse energy can be dialed by means of a combination of a halfwave plate mounted on a computer-controlled rotary stage and a polarizing beam splitter. The laser beam is collimated and expanded by a factor of three before entering the focusing optics (Zeiss Plan Apochromat, NA = 1.4). For sample positioning in 3D space, we use a highly precise air bearing system with a total travel of 15 x 15 x 10 cm³ and sub-micron accuracy (Aerotech ABL1000). For XY translation, the sample is mounted directly on the XY stage combination, while for Z positioning the microscope objective is moved. The patterning process can be monitored in-situ with a CCD camera combined with a dichroic mirror and red light sample illumination.

As photoresists for the fabrication of microstructures, inorganic-organic hybrid polymers (ORMOCER®s) are used. These are negative tone photoresists, i.e., they solidify upon UV or TPA treatment. In comparison to most purely organic photopolymers, ORMOCER®s have superior optical properties as well as very good chemical, thermal, and mechanical stabilities due to their inorganic [-Si-O-]n backbone. They are synthesized from organically modified alkoxysilane precursors that undergo hydrolysis and polycondensation reactions upon synthesis, providing an entire material class as the formation of the reaction products can be modified in a wide range by varying the reaction conditions during synthesis as well as by the choice of alkoxysilane precursors. The reaction products are liquid, consisting of organically modified inorganic networks. The material properties such as, for example optical, mechanical, and chemical functionalization of ORMOCER®s as a material class can be tailored to application specific requirements by the choice of precursors, synthesis and processing conditions. For the presented work, ORMOCER® systems originally developed for applications in microoptics are employed. As organic functional moieties acrylate groups are used. To promote TPA-initiated photopolymerization (and thus solidification), suitable photoinitiators are added to the ORMOCER® resins. For the fabrication of structures, droplets of ORMOCER® resin are placed in between a sandwich of two microscope cover slips, which are separated by a 100 µm thick spacer. The laser pulses are focused on the backside of the first cover slip (substrate), according to the microscope objective’s design conditions. The starting position for 2PP is at the interface of the first cover slip and the ORMOCER®.

It has to be distinguished between two ways of creating microoptical structures using 2PP: For the fabrication of free-standing, arbitrarily shaped 3D structures, the volume of the target structure is solidified by scanning the focal volume through the liquid resin. By performing a subsequent solvent wash (methylisobutylketone:isopropanol - 1:1), only the solidified structure remains on the substrate. For index patterning, the resin between the cover slips is pre-treated photochemically or thermally in order to establish a matrix for the index structures. A solvent wash after the TPA/2PP fabrication is not necessary.

3. RESULTS AND DISCUSSION

3.1 Microlenses

Microlenses are typical structures that can benefit from the freeform capability of 2PP fabrication. However, there are two critical processing constraints, which impede the acceptance of 2PP fabricated microlenses in the scientific community:

1. Throughput - 2PP is a serial process. For this reason, the even the fabrication of microscopic objects can take several hours as the entire volume is typically scanned in a point-to-point fashion.

2. Surface accuracy - For optical applications, a highly precise fabrication of optical surfaces is required. Unfortunately, most papers on 2PP demonstrate particular 3D structures, but there are no extensive studies on how accurately the fabricated shapes actually reproduce the target design.

For increasing the throughput, we developed a new hatching strategy for rotationally symmetric microlenses which combines annular hatching with shell hatching. According to this strategy, only the outer shell of the

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Proc. of SPIE Vol. 9353 93530K-2
desired microlens is solidified by means of 2PP while the remaining liquid core of the lens is treated by UV-flood illumination after the solvent wash. This yields a major process acceleration as only a very small fraction of the entire structural volume has to be scanned point-by-point.

The 2PP shell fabrication is accomplished by annular hatching, meaning hatching the surface by writing subsequent rings with increasing or decreasing radius. The distribution of the rings’ positions, i.e. the radii and heights determine the shape of the lens’ shell which can be spherical, parabolic, linear, or any other desired geometry, and even discontinous profiles are possible to be created. However, fabrication of just a series of rings along the lens’ surface results in strong surface distortions. This is due to the finite acceleration of the positioning system on the one hand, and due to the voxel size (voxel = volume pixel) of 2PP fabrication on the other hand. Both aspects will result in elevations on the lens’ surface: Faster acceleration will lead to extended exposure times at the ring’s beginning and end resulting in larger voxels. Overlapping of voxels at the ring’s beginning and end will intensify this effect. To compensate for these effects, tangential acceleration and deceleration distances combined with precise laser switching using the PSO hardware feature is employed. In addition, the beginning and ending points of the rings are distributed randomly over the lens’ surface.

On the other hand, mere acceleration of the fabrication is pointless if this leads to decreasing surface accuracy. For this reason, the impact of the processing parameters on the formation of the lens’ surface was investigated thoroughly. These are in particular

1. the effect of polymerization shrinkage,
2. the effect of photon dose and hatching/ring distance on the surface roughness, and
3. the effect of photon dose and starting position relative to the substrate.

In contrast to most purely organic photopolymers, the shrinkage upon polymerization in ORMOCER® is comparably small. This can be most likely attributed to the rigid inorganic backbone of the materials class. This effect was investigated for spherical lenses before and after UV flood exposure by means of Atomic Force Microscopy (AFM) as well as Scanning Laser Microscopy (LSM). A small decrease of the lens height, which is strongest in the center and vanishes at their margins was observed. However, as it is significantly smaller than 100 nm, this effect must not be taken into account.

The photon dose, which is brought into the photopolymer is - besides the focusing optics - the most decisive factor for the geometry (diameter and length) of the resulting voxel. It is given by the combination of average laser power or pulse energy and the positioning velocity during the fabrication. The combination of voxel size and hatching distance determines the surface roughness of the fabricated structure. This was investigated by performing AFM measurements on a series of 2PP written 5 x 5 x 5 µm blocks with varying laser power, P, and hatching distance at a constant velocity v = 500 µm/s. By choice of appropriate process parameters, meaning high photon dose and small hatching distances, the resulting surface roughness could be reduced to 3.7 nm compared to several tens of microns for non optimized parameters.

The last relevant effect under consideration is the impact of appropriate photon dose. Only if the voxel size, which is dependent on the photon dose, is infinitesimal small and the starting position of the fabrication was set exactly on the interface between substrate and ORMOCER®, the resulting structure would reproduce the design profile exactly. However, in reality the surface formation is affected by the size and formation of voxels as the surface develops at the top of the voxels and not at their center. To get a closer insight into this, arrays of spherical lenses were fabricated with varying average laser powers and starting positions relative to the substrate. The latter could be dialed by an automatic substrate detection system which was added to our structuring setup.

The laser power was varied from P = 950 µW to P = 1900 µW with an increment of 50 µW, and the starting position was varied from -1.25 µm to 0.0 µm with a 0.25 µm increment. Details on the hatching strategy and the hatching investigations will be published elsewhere.

To demonstrate how the investigations enable the fabrication of smooth and accurate surfaces on small timescales, Figure 1 depicts characterization results for spherical microlenses. The results stem from a lens which was fabricated using v = 500 µm/s and the best combination of laser power (P = 1400 µW) and starting position. This was determined by performing 2D spherical surface fitting to the array of lenses fabricated with varying parameters. According to the design, the lens has a radius of curvature RoC = 45.42 µm. A cross section of
Figure 1. Spherical microlenses fabricated by using an improved hatching strategy. (a) Cross section through the experimentally determined topography and the design (inset: 2D color representation). (b) 2D color representation of surface deviations from the design. (c) Optical image of a fabricated lens array.

the lens’ surface and the deviations from the design data are shown in Figure 1 (a). The inset is a 2D color representation over the entire surface. The plot also depicts a spherical fit through the experimental data for guidance. It can be seen, that the experimental data match the theory almost perfectly. The fitted radius of curvature is 45.24 µm which is a deviation of only 0.4 % from the design. This is demonstrated in more detail in Figure 1 (b) on the basis of a 2D color representation of the deviations from the design function. The RMS deviations are less than 50 nm, which is below \( \lambda/10 \) and to our knowledge a significant improvement for 2PP fabricated microlenses. However, ring shaped surface distortions which might stem from laser power instabilities can clearly be seen in Figure 1 (b). These surface distortions might scatter incoming light and consequently corrupt the focusing behavior of the fabricated lens. This will be investigated in the frame of optical measurements. In conclusion, the adapted hatching strategy and the consideration regarding other fabrication parameters enable a major acceleration for the fabrication of precise microlenses. The time for the fabrication of an individual element is decreased to 1 - 2 minutes using a three axis positioning system without any galvoscariners or other parallelization of the fabrication process. This allows for the fabrication of lens arrays as depicted in Figure 1 (c) (only a small sector of the entire array) in reasonable times which can be even significantly lowered (which will be published elsewhere). The entire array consists of 35 x 35 lenses.

3.2 Diffractive Optical Elements

DOEs for the generation of custom shaped intensity distributions such as multi-spot, line grids, tophat, or other arbitrary distributions are conventionally fabricated by classical two-dimensional lithographic techniques, particularly e-beam lithography. Jia et al.\textsuperscript{28} proposed how 2PP can improve DOE fabrication as its freeform capability enables the realization of continuous height profiles, in contrast to e-beam processing where a single lithographic process step only yields a binary phase or amplitude function. We established another significant enhancement to 2PP DOE fabrication by developing an improved hatching algorithm which allows to utilize much higher scanning velocities, and thus decrease the fabrication time dras-
Figure 2. Height calibration of DOEs. (a) Microscope images of different 16 pixel DOEs (pixel size is 2 µm). (b) AFM characterization of an individual mini DOE. (c) Height distribution of fabricated DOE and DOE design.

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tically. In contrast to previous works, in this hatching scheme the total area of the DOE fabrication is scanned at a fixed height according to the current DOE pixel height. The PSO feature of the positioning hardware only switches the laser if a hatching line hits a DOE pixel, i.e. if the pixel height is higher or equal to the current height during the fabrication process. This is done subsequently for each target pixel height (e.g. 16 phase levels), and allows velocities larger than $v = 1000$ µm/s. Compared to a pixel-by-pixel fabrication approach, in which the entire volume of the DOE pixels is hatched by small XYZ motions, our strategy saves most of the dwell time for repositioning, acceleration, and deceleration of the positioning system, and it results in more accurate pixels.

We first adjusted the design data to the actual height of the fabricated voxels. These can actually be compressed or stretched compared to the programmed target height, as the focusing conditions inside the volume of the photopolymer differ from the design of the microscope objective, and the present refractive index mismatch leads to an axial focus shift.$^{29,30}$ In addition, the focused beam needs to penetrate through already polymerized layers as the fabrication follows an upside down scheme (cf. section 2). This augments the refractive index mismatch and makes thorough calibration even more necessary.

Figure 2. Height calibration of DOEs. (a) Microscope images of different 16 pixel DOEs (pixel size is 2 µm). (b) AFM characterization of an individual mini DOE. (c) Height distribution of fabricated DOE and DOE design.

Mini DOEs consisting of 16 pixels according to 16 height levels were fabricated using different distributions of the pixels in each mini DOE in order to determine the best parameters for large-scale DOE fabrication. The maximum design height is 1.5 µm corresponding to 100 nm increments between axial layers of the DOE. Figure 2 shows microscope images of four exemplary mini DOEs (a) and the results of a single LSM measurement of a mini DOE (b). Finally, Figure 2 (c) depicts the analysis of 16 mini DOEs. It can be seen, that the fabricated pixels (red bars) are compressed compared to the design (black bars). Linear fitting delivers a compression ratio of 86.74 %. For this reason a correction factor of $1/0.8674 = 1.153$ was taken into account during a next iteration of mini DOE fabrication. Analog analysis of the resulting pixel heights of the pre-corrected designs revealed good agreement between design height and pixel height. Consequently, this correction factor was fed into the fabrication of larger DOEs. Figure 3 (a) depicts a microscope image of a section of a larger quasi-random DOE and corresponding LSM characterization is shown in Figure 3 (b). It was fabricated using a scanning velocity of $v = 1000$ µm/s and an average laser power of $P = 900$ µW in less than 10 hours. The entire size of the DOE was $1024 \times 1024$ µm².

The next task currently being executed is to fabricate a functional DOE using the new hatching strategy (PSO with correction factor) which relies on computer-generated phase patterns for specific diffraction of light into a desired distribution. Optical characterization of this large DOE (e.g. $2 \times 2$ mm²) will be reported as well.
3.3 Index Patterning

The patterning of index structures in polymeric matrix materials can pave the way to new device concepts in integrated opto-electronic devices. Particularly applications in optical interconnects for data transfer (chip-to-chip or chip-to-fiber), where TPA-written structures act as optical waveguides are highly appealing. In this concept, polymerization in the focal volume induces a local boost of refractive index, allowing for the fabrication of 3D optical waveguides by scanning the focal region on an arbitrary trajectory. In comparison to classical waveguide fabrication using UV patterning, this enables the establishment of optical links between components such as laser/photo diodes and fibers in significantly fewer process steps. Thus, resources are saved and the alignment of the components to be connected is not critical as the waveguide is written after their assembly, and its path can be adapted to their location. In most current demonstrations of this concept the geometry of the fabricated waveguides or waveguide bundles is determined by the geometry of the focal region. As mostly low NA focusing optics are employed, the profile of the waveguides is either elliptical or has to be shaped by external compensation optics. Figure 4 shows very recent results of index patterning using the same high NA focusing objective, which is used for 2PP patterning of microstructures. Here, the voxel diameter is much smaller than the desired waveguide profile. This enables the fabrication of custom waveguide shapes by hatching the waveguides cross section in an adapted way.

To evaluate the processing parameters, arrays of 75 µm long waveguides were fabricated with perpendicular orientation to the substrate. The hatching distance is $\Delta x = 250$ nm, the writing velocity $v = 100 \ \mu m/s$ and the average laser power was varied from $P = 1300 \ \mu W$ to $P = 2200 \ \mu W$ in 100 $\mu W$ increments (from top to bottom). The potential for tailoring the waveguide’s geometry is demonstrated not only by realizing different waveguide sizes (singlemode vs. multimode), but also by changing the shape of the waveguide. We could fabricate circular,
square and elliptical (aspect ratio e.g. 3:1) waveguide shapes, just by adapting the computer design and thus altering the hatching of the waveguide’s cross section. Furthermore, is it also possible to alter the gradient of the refractive index of the waveguide: Simple hatching of the waveguides’ cross sections results in a step index profile. However, the boost of the refractive index is determined by the photon dose applied during hatching. Consequently, gradient index waveguides can be fabricated by adapting either the velocity or the laser power during hatching. For demonstration, an array of gradient index waveguides was fabricated in which the average laser power was decreased by 1000 $\mu$W from the center to the margin of the waveguide. As obvious from Figure 4 (c) this decrease in power was not sufficient to create a smooth index gradient. This is presently investigated in more detail, and the results will be published elsewhere.

For 2PP fabricated waveguides, it is decisive that the contrast in refractive index between TPA-treated structure and matrix remains at long time scales. A qualitative demonstration for this was conducted by exposing the sample to ambient light for several weeks. No alteration in image contrast before and after exposure could be observed by optical microscopy in transmission mode. However, further extensive studies on the influence of UV- and temperature treatment need to be carried out in the future. In addition, optical, refractive index and mode field characterization is essential for a better understanding of the underlying photochemical processes and for the transfer to a real world application.

4. SUMMARY

2PP technology can enhance the performance of microoptical components and enable new device concepts due to its freeform capability and the possibility to perform refractive index patterning. Microlenses, DOEs, and waveguides, were discussed and the particular benefits from 2PP in these examples were illustrated. By employing adapted hatching strategies such as shell/annular hatching with acceleration and deceleration distances and exploiting the potential of the air-bearing positioning system (high velocity compared to piezo, PSO-feature), a major step for higher throughput and the implementation of 2PP for other applications could be taken. Furthermore, a prerequisite for this in the field of microoptics is a better understanding of the structure formation and the influencing processing parameters in terms of (surface) accuracy. This was elaborated for spherical microlenses and the pixels heights in DOE fabrication. In the field of index patterning the fabrication of waveguides with different cross sections and tailored index of refraction is possible. However, in further experiments thorough optical characterization of the fabricated elements is necessary in order to prove the advantageous of 2PP written structures and pave their way into functional devices.

ACKNOWLEDGMENTS

The authors highly acknowledge the support and constructive discussion of the colleagues in Jena and Würzburg. We also thank the German Science Foundation (DFG) for funding in the framework of their Priority Program SPP-1327 (grant: HO2475/3-1).

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