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Insights into challenges and potentials of two-photon lithography

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Abstract
In the last decade, additive manufacturing has enormously developed. With a growing range of technologies, an expanded material portfolio, significantly increased reproducibility, and an increasing precision, it overcame the threshold from pure prototyping towards its use in real production. However, the new possibilities also brought challenges. On the one hand, there is the need to discuss the exploitation of opportunities as well as potential complex components. On the other hand, the metrology is still an incompletely solved issue.

With two-photon lithography (TPL), an additive process is available whose precision exceeds the diffraction limits of conventional laser lithography systems and, at the same time, allows the production of 3-dimensional components. Using conventional resists and specialized materials, such as organically modified ceramics, micro-mechanical, micro-fluidic, refractive and diffractive micro-optical systems can be realized. In recent years, the technology has shown its potential regarding various fundamental applications and it is on the transition to an industrial integration. The paper provides insights into the potential of this technology that is used during real production and the emerging challenges for the precision community during the transition period towards integration in manufacturing chains. Selected components are introduced, e.g. from micro cytometry and diffraction optics. Furthermore, the use of standard components intending to classify the precision of TPL systems is discussed.

The system presented here comes with several harmonic generators, providing a wavelength range from the IR to the UV. Thus, the system is able to combine classical laser micro-beam technologies, such as ablation and single-photon lithography, with the potentials of two-photon lithography. Hence, it enables micro-products with significantly advanced precision in the future.

Keywords: micro production, lithography, 2pp

1. Introduction

Two-photon polymerization (2PP) has been used for the production of photonic crystals for two decades [1]. Over the years, it has developed into a scientific tool to produce three-dimensional microstructures. Commercial systems have been available for more than a decade, which, in addition to scientific use, allow the transition to industrial use.

The 2PP works by irradiating the resist to be polymerized with a source whose wavelength provides only half the energy necessary to activate the photoactive component. Thus, two photons must be absorbed almost simultaneously. However, this is only sufficiently probable at very high temporal and spatial photon densities. The material dependence is given by the so-called material specific cross section in the unit Göppert-Mayer, in short GM. The unit was named after Maria Göppert-Mayer, who for the first time described two-photon absorption theoretically [2]. The necessary photon densities are achieved in the focal region of a laser beam. Due to the energy distribution in the Gaussian distributed focal region, a defined elliptical volume unit (voxel) polymerizes, with a size below the diffraction limit. By moving the focus within the resist and thus assembling voxels with the help of the pulsed laser, three-dimensional structures can be created.

Various materials with different properties are available today, allowing the technology to be used for a wide range of applications. Existing UV negative resists like SU8, but also optically and mechanically optimized OrmoCer (organic modified ceramics) up to soft materials like PDMS [3] can be structured. By means of parametrizing the laser that interacts with a suitable material, even property gradients within the material can be generated [4]. Therefore, applications are to find in all fields of microtechnology, e.g. micro-fluidics [5], micro-optics [6, 7], and microengineering [8].

Due to the diversity of materials, various structural requirements, and precision demands, different writing modes have evolved. It is possible to pattern in immersion as well as with larger working distance. In addition, liquid resists or resists solidified by annealing can be developed. It is also possible to expose the resist through glass slides.

2. System and Material

The system used here is a customized FemtoLAB laser workstation, made by Workshop of Photonics (Lithuania). Starting from laser wavelength 1030 nm, the system generates the wavelengths 515 nm and 343 nm using harmonic generators. This enables 1PP, 2PP, and ablation in one setup.

The system comes with an XYZ precision stage positioning unit and a galvo scanner. These provide optimal writing processes by means of their independent or simultaneous use. In simultaneous operation, the so-called infinite field of view technology achieves a synchronization of the two systems, so that stitching is prevented when writing field sizes that exceed the writing range of the galvo scanner.

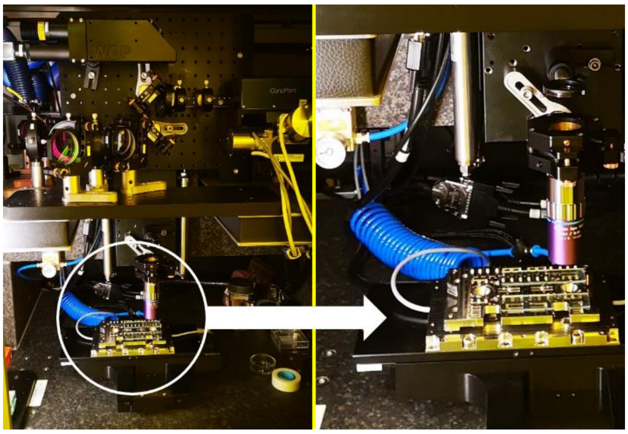

Figure 1. Inside view of the 2PP lithography system

The material used for the experiments is OrmoComp© by microresist Technology GmbH (Germany). The material shows glass-like properties after development. It is, therefore, particularly suitable for optical applications, but also enables mechanical applications.

Table 1 OrmoComp© properties

viscosity [Pa·s]	2.0 ± 0.5
curing wavelength [nm]	300 – 410
recommended exposure dose [mJ/cm²]	500 – 1500
shrinkage [%]	5-7
refractive index (cured, 589 nm)	1.520
Abbe number	47
CTE (20-150 °C) [ppm/K]	150
dn/dT [10^{-4}/K]	-2.0
Young's modulus [GPa]	~1
hardness	
via indentation [MPa]	~68
Shore D	75

3. Technological challenges

3.1 Procedure

The writing speed and the quality of the result are influenced by the 2PP process parameters as well as the writing strategy. Both must be weighed against each other. For the writing process, the galvo scanner and the precision positioning unit are basically available. The galvo scanner is characterized by high writing speed and precision, but has only a very limited field of view (FoV), which varies depending on the objectives. The higher the targeted precision, the larger the required numerical aperture (NA), and the more limited is the FoV.

Thus, to produce features that are significantly larger than the FoV, the stage positioning unit must be moved. In the case of sequential movement, exposure is performed locally using the galvo scanner. The stage moves to a programmed position and the galvo scanner operates again. In this case, the positioning inaccuracy, as well as possible volume shrinkage effects of the resist, lead to stitching effects, which cause structural flaws. Depending on the structure, these imperfections may only be an aesthetic problem, or they may compromise the function. To avoid such imperfections, the positioning unit and galvo scanner work synchronously.

Regardless of the used motion strategy, different basic writing strategies are available (see Figure 2. a-c). Analogous to macroscopic additive manufacturing processes, the structures can be completely polymerized level by level after being sliced. In this case, the entire volume must be polymerized during the writing process. This process is very time-consuming. Alternatively, especially in this additive process, only the shell of the component can be polymerized with 2PP. In this case, liquid resist is enclosed in the shell. The enclosed resist can be completely polymerized in a following step by means of a UV flash with 1PP.

This procedure is the fastest option for creating large-volume components. However, the volume shrinkage during UV flash strongly affects the quality of the resulting product.

An intermediate approach is the use of additional support structures. Here, hatching-like structures support the shell and enclose several separate liquid resist volumes that are polymerized through a subsequently performed UV flash. The hatching structures are no longer visible after polymerization but can locally influence the material shrinkage. By using hatching structures, a compromise of time and precision can be achieved.

Figure 2. Exposure strategies: a: fully exposed, b: only shell exposed, c: shell and hatching structures exposed

As structures grow larger, such compromises become increasingly important. Even if stitching marks do not occur along the writing trajectories due to synchronization, further problems can arise when writing large-scale structures. No matter how the writing strategy is chosen, depending on the structure it is sometimes unavoidable that certain workpiece areas have to be passed twice. At these intersection areas, overlapping phenomena can occur. For example, local material shrinkage can result in visible shrinkage marks. The influence of these marks on the workpiece quality depends on the strategy, the material and the voxel size. Figure 3 exemplarily shows a trajectory that can lead to such an intersection mark.

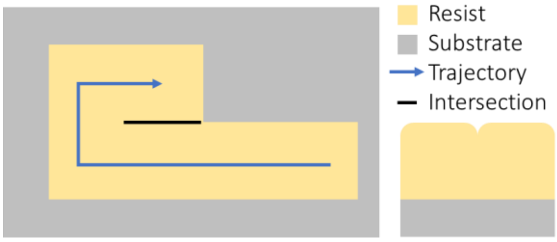

Figure 3. trajectory that can cause an intersection mark

A feature oriented writing strategy is to choose that avoids intersection marks as well as stitching marks or permits them only in areas that are functionally.

3.2. Upscaling

Many published application examples address nm-scale features, especially structures that can be written within the FoV of a galvo scanner. These small structures with a level of detail in the sub-micrometer range are definitely a unique selling point of this technology. However, there is a gap between this technology and other additive processes such as stereolithography (STL). Structured areas that are too detailed for STL but too large in for 2PP are not adequately covered. Therefore, upscaling strategies are necessary in the long term.

One example of upscaling is the prototyping of micro-fluidic structures. Figure 4 shows in detail the hydrodynamic focusing of a micro-cytometer developed by the MFG and Physikalisch-Technische Bundesanstalt (PTB, Germany). The fluidic swirl focuses blood platelets for subsequent size measurement. The original prototyping consists of a sophisticated process chain based on ultra-precision machining. In particular, the sealing of the microchannels of this multilayer structure is complex. By means of 2PP, such structures can be manufactured directly, also as closed cavities.

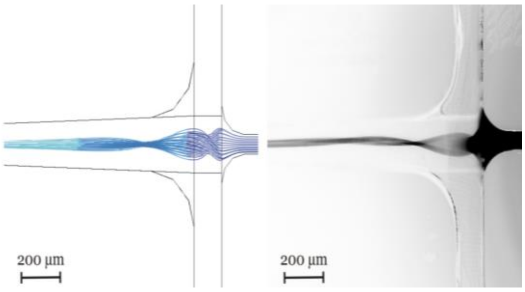

Figure 4. Micro fluidic hydrodynamic focusing invented by TU Berlin and PTB [9]

Direct miniaturization of such structures by 2PP is possible. Figure 5 shows a half-section of the cytometer as a 20x downsized component.

The challenge, however, is upscaling those features with acceptable production times, reliability and maintaining precision in different polymers.

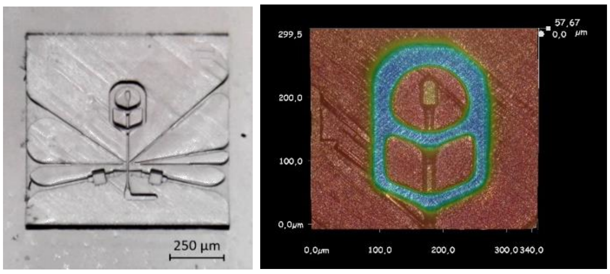

Figure 5. fluidic structure [9] 20x miniaturized (left) and example measurement (right)

4. Test component

In conventional mask-based 1PP UV lithography, the achievable resolution is approximated by simple diffraction considerations using the Rayleigh criterion. In 1:1 shadow exposure it is limited by near-field diffraction as a function of wavelength, resist thickness and proximity distance. In the case of projective exposure, it is limited by the wavelength, the NA and the respective correction constant of the used optics. Experimentally, the resolution can be determined by simple comb structures with variable spatial frequency. The parameter space of the 2PP is much more complex, furthermore an evaluation in three-dimensional domain has to be done, which causes additional metrological challenges.

In the context of multi-axis simultaneous machining, test components are required which allow the performance and quality of the systems to be objectively evaluated and compared. An initial test component is presented here, which is to be extended in the future by further useful structures, which in particular consider the degrees of freedom of 2PP technology. The test component contains macroscopic structures as well as microstructures, e.g. blaze gratings. The macroscopic structures have several levels, so that centricity and height can be detected, additionally. Some features are repeated in order to be able to evaluate their position to each other. In addition, features were integrated that cannot be written in a single trajectory, so that overlapping areas are forced even when the galvo scanner and positioning unit are synchronized. The individual structures are located on a solid base body. A CAD auf the initial test component is shown in Figure 6. A processed OrmoComp© part and a three-dimensional measurement can be seen in Figure 7.

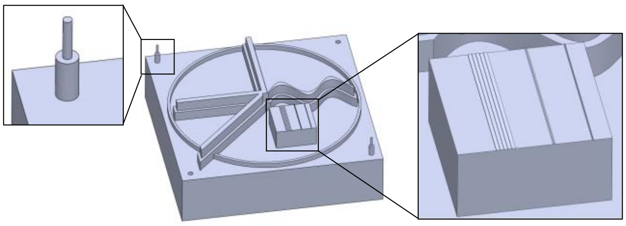

Figure 6. CAD and details of the test component

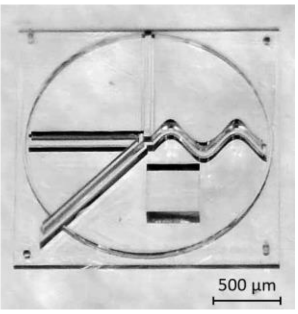

Figure 7. Test component made from OrmoComp©

The component initially addresses the dimensional measuring of tolerances. In the future, it will be supplemented by functional structures to be able to record the quality indirectly as well.

5. Procedure and results

5.1 Procedure

As described, various configurations are available for the exposure of the resist. These can also be implemented in the system used. The configuration used for the experiments is shown in Figure 8. In order to fabricate large-area structures in a time-efficient manner, a Mitutoyo 50x / 0.42 objective was used. This objective is not used in dip-in, but with a working distance. Since the resist used is liquid and to exclude influences of an uneven surface, the resist was enclosed between two precision cover glasses with a defined distance.

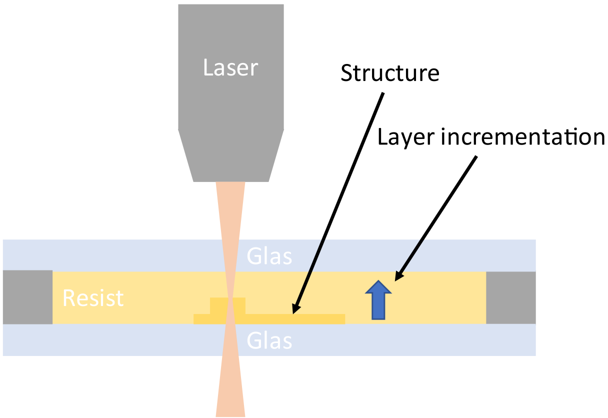

Figure 8. schematic illustration of the exposure configuration used

The following basic parameters are used:

- Laser: 601.8 kHz, 515nm
- Position Synchronized Output (PSO) 10k/mm
- Laser power Controller 25%, Attenuator 40%

In this case, the writing process starts from the surface of the lower glass to ensure that the structure is bonded and built up layer by layer. This may be necessary for liquid resists.

Different writing strategies, full polymerization, partial hatching, and large-scale hatching, were carried out. The layer wise and feature oriented mixture of these methods was also considered. The production times varied between 5 and 10 h.

5.2 Results

An exemplary production result is shown in Figure 7. The results were subsequently observed via microscope (Figure 9) and measured via digital microscope Keyence VHX 2000 (Figure 11) and individual achievable surface defects via Nanosurf Nanite AFM (see Figure 10). A comparison of the structures with and without defect marks can be seen in Figure 9. These surface defects can extend to several micrometers but can be strategically avoided.

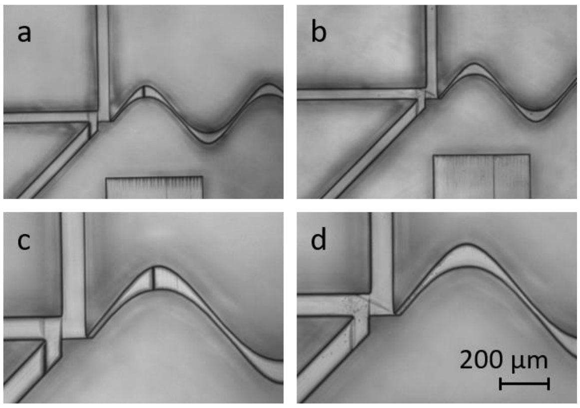

Figure 9. Microscope image of test structures: a and c with, d and d without surface defect marks

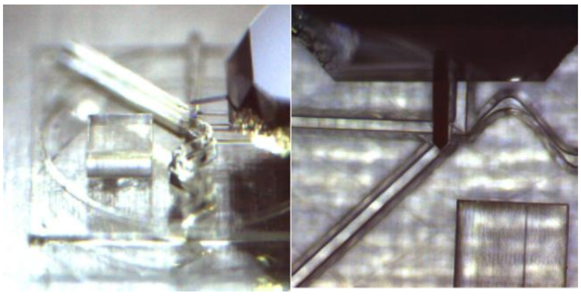

Figure 10. AFM measurement of surface defect marks

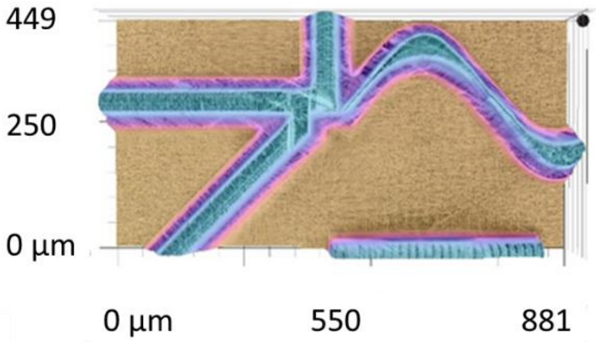

Figure 11. Measurement of test features

However, this requires an individual strategic adjustment, which was carried out iteratively for some sections.

Figure 10 shows detailed images of corresponding sections of the test component with and without defects.

The results are in the sub-micrometre range despite the intended rough voxel structure with the low NA and the chosen parameters, which is due to the temporal optimization. Further experimentation and scaling of the component to use different NA up to immersion, as well as inclusion of new features, will be focused in future activities.

It has been shown that even when creating parts that extend far beyond the field of view of a galvo scanner, synchronization and strategic interventions can enable structures that are highly accurate without stitching and intersection marks.

6. Discussion and outlook

The many international publications of the last decade have shown that the 2PP is of high potential for additive manufacturing in microtechnology. During the transition of this technology from a prototyping tool to a production process as well as during the upscaling of the component sizes, methods are necessary to ensure the process reliability and to evaluate performance objectively. The work presented here contributes to the creation of necessary test components.

However, the potential of the technology goes beyond the dimensions that can be tested here.

Based on this work and in collaboration with the additive manufacturing as well as the metrology community, these methods will be extended in the future.

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