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Precise structuring by 2-photon absorption in positive photoresist materials

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Abstract

Two-photon polymerization, based on two-photon absorption, is a convenient direct laser writing process to fabricate maskless structures in micro- and nanometer range with submicrometer resolution. Negative photoresists are used in combination with this technique, however, utilization of positive resists with two-photon absorption is very innovative. Due to less shrinkage and economic manufacturing, positive photoresists have many advantages. Possible applications of this technique are the production of micro-electro-mechanical systems (MEMS) or micro-opto-electro-mechanical systems (MOEMS). In this paper, two-photon absorption of positive photoresist is discussed to be a potential basis for LIGA-process (lithography, electroplating, and molding) by two-photon absorption of positive photoresist is discussed. The maskless ultra short pulse illumination by femtosecond laser pulses with 780nm wavelength for generation of microstructures in positive photoresist is demonstrated. To assure high quality structure surfaces, the influence of processing parameters on the pattern width are studied. Therefore, the influence of average power of femtosecond laser pulses, as well as the influence of the scan velocity on the resolution for 3D-grid structure is experimental tested. These studies enable fabrication of arbitrary 3D-structures with high resolution and high aspect ratio. By utilizing a commercial positive photoresist, a minimum linewidth in submicron order with essential rise of the aspect ratio has been accomplished. Furthermore, the test of a precise structuring of complex geometry fabrication is presented with an elastomeric molding. Based on these results, the application possibility for LIGA-process is demonstrated.

Keywords: positive photoresist, two-photon nanolithography, LIGA

1. Introduction

Direct Laser Writing (DLW) is a convenient process for maskless fabrication of arbitrary three-dimensional (3D) micro- and nanostructures in negative photoresists with lateral dimensions below 100 nm [1, 2, 3, 4, 5]. These structures are used in medical and biological devices [6, 7] or optical devices like lenses and mirrors [8, 9]. Additionally, negative photoresist doped with metal nanoparticles or carbon nanotubes are used to generate conductive nanostructures for MEMS or MOEMS applications [10, 11].Besides negative resist, positive resists are more commonly used for the fabrication of electrical conductors, lab on chip or other applications. The utilization of positive photoresist in DLW and the implementation of two-photon absorption (2PA) enable the fabrication of various 3D microstructures [12, 13].

LIGA (lithography, electroplating and molding) is a fabrication process for MEMS and MOEMS. Photoresists are structured by synchrotron radiation. This technique offers precise manufacturing of microstructures with high aspect ratios of more than 100 [14, 15, 16]. However, the fabrication setup is very expensive and complex because of the need

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for a vacuum chamber for x-ray radiation. Additionally, ultraviolet (UV) - light can be used to perform LIGA. Nevertheless, the fabrication of complex geometries is limited due to the application of masks.

2PA with positive photoresists offers an alternative process for LIGA with high resolution and low production time. In this paper we study the dependency on linewidth for high precision structuring and for the use of flexible elastomer instead of electroplating. Thereby we will demonstrate the feasibility of this method.

2. Materials and methods

2PA is a quantum mechanical three-body process, which describes the simultaneous absorption of two photons [18, 19]. With the absorption of the first photon, a virtual state is formed, which has a lifetime of several femtoseconds. Therefore, 2PA is only possible if a second photon is absorbed before the virtual state decays. The energy of one photon is given by $E = hv$, where h indicates the Planck constant and v the frequency of light. Thus, energy for one excitation event by absorbing two-photons is given by $E = 2hv$, the sum of both photons energies. With the utilization of an ultrashort pulse laser the non-linear absorption occurs only in the volume of the focus (voxel). In this area, the quantity of quasi simultaneous photons is sufficient high to initiate the non-linear process. The absorption of two photons within positive photoresist induces a photochemical change. As a result, these illuminated areas can be removed by the developer. (Vice versa, for negative photoresists the non illuminated area is removed by the developer.)

Positive photoresists generally consist of a resin and a photo-active component (PAC). The resin is a Novolac whose matrix consists of an OH-substituted aromatic benzene ring. The matrix represents the solid structure of the photoresist. The PAC is responsible for the insolubility of the Novolac resin before the exposure and increases the solubility of the resin. The PAC is the hydrophobic Diazonaphtoquinone (DNQ) which prevents attachment of water to Novolac. The matrix of the DNQ is a naphthalene molecule, but the chemical and physical behavior of the chemical bond are affected by substituents. All aromatic compounds strongly absorb UV-light near the visible light. By adding a substituent it is possible to shift the absorption spectrum to a higher wavelength, whereupon not only the chemical composition of the substituent affects the wavelength shift but also the position the substituent is connected to the aromatic compound. In this work, the photoresists ma-P 1225 and ma-P 1275 (micro resist technology, Germany) are used. These are commercial broadband positive resists with high absorption coefficients at wavelength between 300 nm and 450 nm.

3. Experimental setup and sample preparation

The positive photoresists require proper preparation steps to ensure precise structuring. First, we use spin-coating of the photoresist on a cover slip. The layer thickness of ma-P 1225 is 3.5 µm at a rotational speed of 2000 rpm and 30 s and 7.5 µm for ma-P 1275 with a rotation speed of 3000 rpm and 60 s. A softbake on a hot plate at 100 °C for 1 minute (ma-P 1225) and 5 minutes (ma-P 1275) is accomplished to reduce the amount of solvent and water in the composite. However, water is required for the conversion of DNQ-acid into carboxylic acid. Finally the sample is rehydrated by exposure to the humid air with humidity higher than 40 % at room temperature.

For the 2PA process we use a mode locked Ti:sapphire laser system (Tsunami, Spectra Physics), with a repetition rate of 82 MHz, pulse width of 90 fs and a wavelength of 780 nm. A schematic illustration of the experimental setup is presented in figure 1(A). The laser beam power can be controlled through a rotating λ/2-plate and a polarization beam splitter cube. An acousto-optic modulator (AOM) is employed as a fast shutter. The substrate coated with positive photoresist is positioned with a mechanical stage (ANT 130-XY and Wafer Max Z, Aerotech). The expanded laser beam is focused by an oil objective lens with high numerical aperture (100x magnification, NA = 1.4). Data files in STL-format assured the writing of arbitrary structure forms. The arbitrary structures are written by scanning the photoresist using a 2D galvonoscanner. After each layer, the sample was shifted along the z-axis by the mechanical stage to get a three-dimensional structure. The written structures are developed for 50 seconds or 80 seconds depending on the layer thickness in an aqueous NaOH-based solvent ma-D 331 (micro resist technology, Germany). The sample is air-dried to evaporate the developer afterwards.

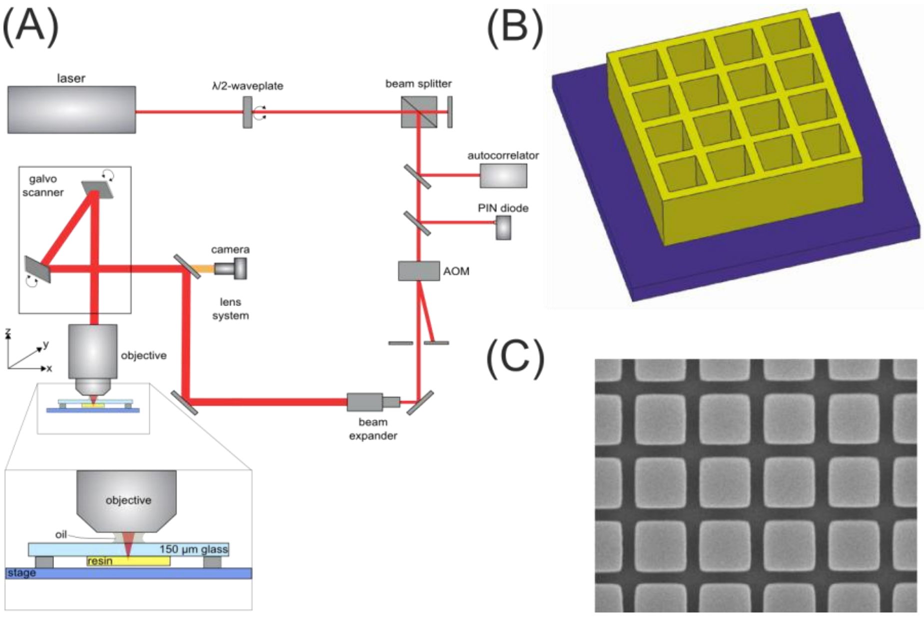

Figure 1: **Experimental setup for two-photon absorption and structure pattern.** (A) Experimental setup for 2PA. Average pulse power is controlled by a rotating λ/2-plate and a polarization beam splitter. An AOM is used as a fast shutter. The expanded laser beam is focused by an objective lens through a cover glass with 150 µm thickness into the positive photoresist. (B) CAD-Model of the grid structure. (C) SEM picture of a negative grid structure written in the positive photoresist ma-P 1225. Top view shows the blocks between the lines.

The validation of the structure quality occurs with an elastomeric molding instead of electroplating due to the fact of availability, simple operating and avoiding electrodeposition. Nevertheless, the fabrication of high quality elastomeric moldings requires defined processing steps. In the first step we mix the components of the elastomer in the right ratio. Unwanted air in the mixture is removed by a venting process in a vacuum bell jar. The elastomer is given to the structured photoresist afterwards. Another venting process in vacuum removes gas and air pockets out of the sample. At last we bake the sample in an oven at 80°C for 6 hours following by cooling at room temperature. The elastomer can be removed.

4. Results

For the purpose of high-precision microstructure fabrication with 2PA a small linewidth is from major importance. Hence the influence of pulse average power and scanning velocity (of the galvoscanner) on the quality of the written structures and on the size of linewidth was studied. Therefore a grid structure as shown in Figure 1(B) was written in ma-P 1275 and developed. The overall grid structure size was 30 µm^2. The distance between the lines was 5 µm. The scan velocity was locked to 0.95 mm/s. The thickness in z-direction was defined with 500 nm to get straight edges of the grid structure. The measurement of the linewidth was accomplished using a scanning electron microscope (SEM). Figure 2(A) presents the influence of average laser power on the linewidth.

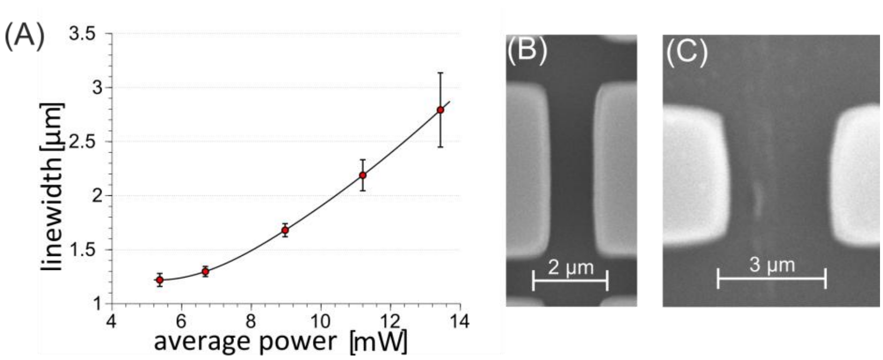

Figure 2: **Size distribution of the linewidth against average laser power.** (A) The scanning speed was 0.95 mm/s and the distance between the lines was 5 µm. The number of layers was 10 with an increment of 500 nm in z-direction. An SEM is used to measure the linewidth at the top of the structures. (B)-(C) presents the results of the effect of increasing laser power to the size of linewidth.

At an average laser power of 5.4 mW, the average linewidth was 1.22 ± 0.05 µm. By increasing the average power, the average linewidth increased. A result of a high quality structuring with almost straight edges is presented in Figure 2(B). The structure was written with an average power of 5.4 mW. The quality of the structure decreases by increasing laser power. The edges of the structure in Figure 2(C) offered high burrs. The average power for the process was 13.4 mW and induced a linewidth of 2.79 ± 0.3 µm. A further increasing of laser power was unfeasible due to micro explosions in the photoresist.

Subsequently, the influence of the variation on the scanning velocity was studied. Compared to the previous experiments the size of the grid structure and the layer thickness was kept constant. The average power was locked to 5.3 mW. Figure 3(A) presents the dependency of linewidth on the scan velocity.
In contrast to the study on linewidth with the variation of the average laser power, the minimum linewidth was in submicron range. Nevertheless, the same effect as in the previous experiments can be found concerning the grid shape. The structure had burred edges at the lowest scanning velocity of 0.38 mm/s with an average linewidth of 1.90 ± 0.12 µm as presented in Figure 3(B). A further reduction of the scan velocity implicated micro explosion in the photoresist. High quality structures were produced with high scan velocity (Figure 3(C)). The minimal archieved linewidth for the average power of 5.3 mW was 0.86 ± 0.12 µm with a scan velocity of 1.9 mm/s.

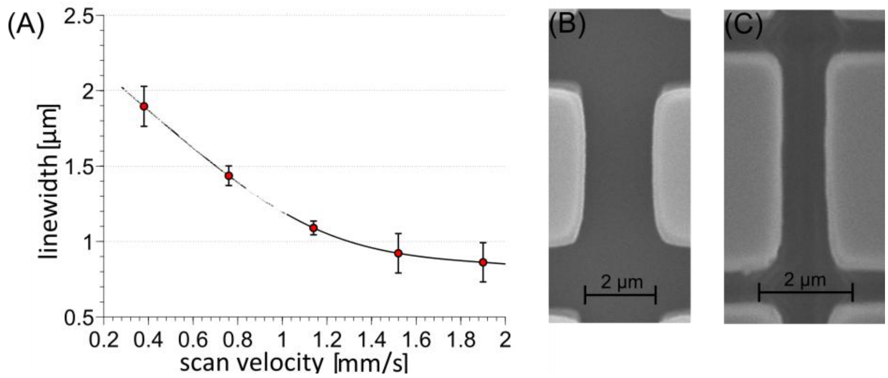

Figure 3: **Size distribution of the linewidth against the scan velocity.** (A) The average laser power in this series of measurement was 5.4 mW, the distance between the grid lines was 5 µm. Linewidth was measured by SEM at the top of the structures. The linewidth decreased from 1.9 µm to 0.86 µm. (B)-(C) presents, that not only the linewidth, but also the amount of burr decreases with an increasing scan velocity. At a scan velocity of 0.38 mm/s, the linewidth is 1.9 µm (B) and decreased to 0.86 µm at 1.9 mm/s (C).

For the LIGA process, the aspect ratio and quality of structures are in the focus of interest. The structures, presented in Figure 4, were produced in ma-P 1275 with a scan velocity of 1.5 mm/s and an average laser power from 7.7 mW to 7.9 mW. The distance between two blocks at the bottom was between 1.3 µm and 1.6 µm. These results exhibited a maximum aspect ratio of 18. The T-top form of each structure block is conspicuous. The disturbing form directly depends on the chemical characteristics of the positive photoresist and has to be investigated separately.

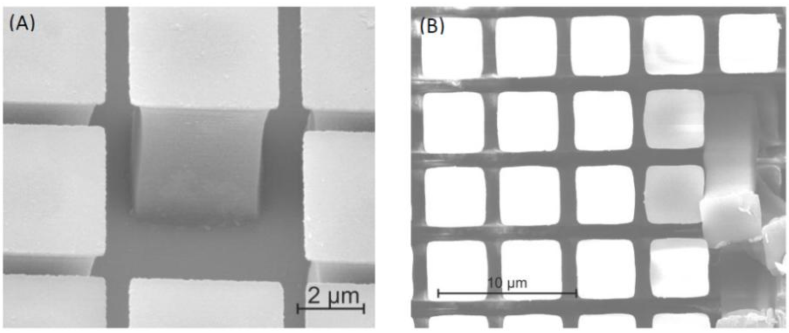

Figure 4: **SEM images of a negative grid structure.** (A) The layer thickness was 7.5 µm and the distance between two structures at the bottom is 1.3 µm. The scan velocity was 1.5 mm/s and average laser power 7.9 mW. The T-top of the structure is very conspicuous, so that the distance at the top of the blocks between two structures is only 650 nm. (B) The layer thickness is 30 µm and the distance between two structures at the bottom is 1.6 µm, which results in an aspect ratio of 18. The scan velocity was 1.5 mm/s and average laser power 7.9 mW.

The previous results provided a basis for the maskless fabrication of three-dimensional complex structures with 2PA. In further experiments frustums were written in the positive photoresist. The slope was 46 degrees, the average pulse power was adjusted to 10 mW and the scanning velocity was 0.5 mm/s. The shape of the written strucutre and the step size in z-direction of 1 µm are presented in Figure 5(A). As a result, the thickness of each layer in z-direction can be seen and is related to a low structure quality. A low quality of the surface texture in the positive photoresist has an effect on the roughness of elastomeric molding.

Using the latest results of linewidth optimisation increased the quality of 2PA structures including the quality of elastomeric molding in further experiments. Figure 5(B) shows high elastomeric molding of a pyramid and a frustum. Precise structuring and high quality are proved for geometries with high slopes. The slope for both structures was 46 degrees. The average power was 7.7 mW, the scan velocity was 0.3 mm/s and the step size was defined to 0.9 µm.

However, an array structure with a pyramidal form was fabricated additionally with one 2PA-writinig process and one elastomeric mold (Figure 5(C)). In contrast to the previous structures, shown in Figure 5(B), the slope of the pyramids was even higher (72 degrees). The structures were written with an average power of 8.5 mW and a scanning velocity of 0.4 mm/s. The step size in z-direction was adjusted to 1 µm.

Finally a complex geometry in the form of a twisted truncated pyramid was written in the positive photoresist and was elastomeric molded. The edge length of the base area is 50 µm.

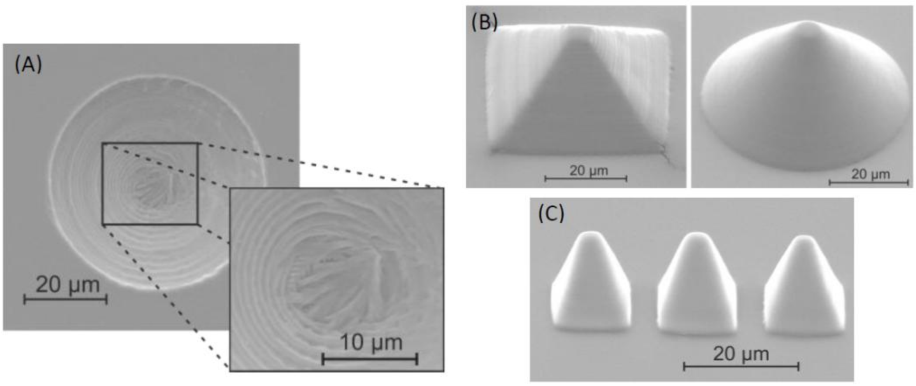

Figure 5: **SEM images of a negative structure and elastomeric mold structures.** (A) A low quality negative structure of a frustum, which generated cracks in the molding. The slope of the frustum was 46 degrees. (B) High quality molding structures of a pyramid and a frustum by changing the average laser power and scan velocity. (C) Generation of a pyramid array with one molding process.

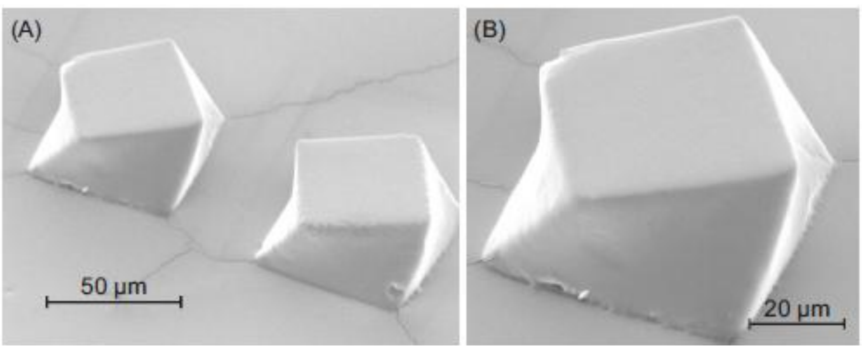

Figure 6: **SEM images of a twisted truncated pyramid structure.** These structures were elastomeric molded. The upper surface is twisted around about 45 degrees. The edge length of the base area is 50 µm. The edge length of the upper base area was defined to three-quarter of lower base area.

To assure a high quality elastomeric molding the edge length of the upper base area was defined to three-quarter of the lower base area. In comparison to the lower surface, the upper surface is twisted around about 45 degrees. Fabrication of precise structure forms required a low average power of 5 mW. The scan velocity was 0.1 mm/s and the step size was 0.8 µm. As a result, precise structuring by 2PA for complex geometries is presented in figure 6 by high quality elastomeric molding with low roughness of the surface.
In addition, figure 7 shows the written structure in positive photoresist with considerable residual of the elastomer.

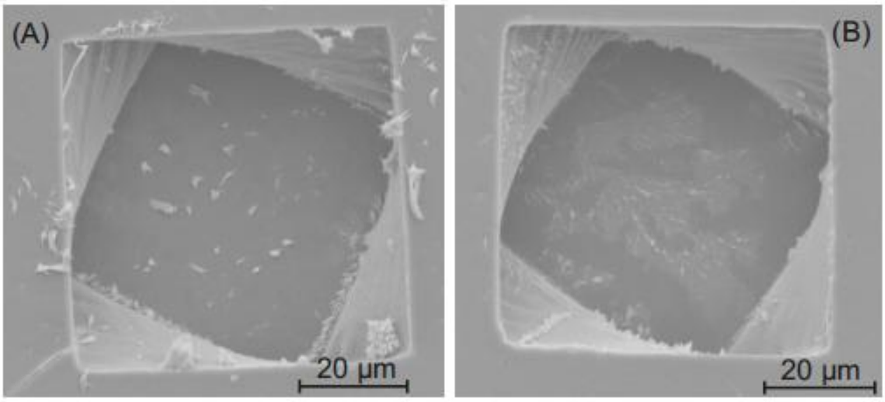

Figure 7: **SEM images of twisted truncated pyramid structure in positive photoresist**. The scan velocity was 0.1 mm/s. The average laser power was 5 mW. (A) shows considerable residuals of the elastomer from the molding process. (B) presents a superior molding quality in contrast to (A).

5. Discussion

The results show application possibility for LIGA process with 2PA, especially for the fabrication of precise structures. High quality fabrication requires an experimental study of dependency of linewidth, which relates to the resolution of structuring with 2PA. In addition, the influence of pulse average power and scanning velocity on the quality of the written structures is experimental established. The increase of scan velocity and the reduction of average pulse power decrease the linewidth due to a smaller voxels. Thus, fabrication of structures with submicrometer resolution can be realized with 2PA. The fabrication of T-tops in the positive photoresist can be identified in further experiments, especially for the investigations of the maximum aspect ratio with 2PA and positive photoresists. This disturbed T-top shape of the structure attributes to the change of consistence at the edge of the photoresist, which exihibts a different chemical character. Another severe disadvantage is the low aspect ratio, which can be reached with 2PA in contrast to UV-light or synchrotron radiation due to the instability of the positive photoresist.

Moreover, the validation of LIGA-process for complex geometries was realized with an elastomeric molding due to availability and simple operation. The received quality of molding with this material was sufficient high enough to confirm the application of 2PA for LIGA. Occasionally, cracks could be identify on the elastomeric structures, which formed by the molding process (Figure 6(A)). In addition, elastomeric residuals were in the negative 2PA-structure after the molding. With the utilization of electroplating, these defects would be removed. Maskless arbitrary processing with 2PA-technique for the LIGA-application was demonstrated by the fabrication of twisted structures and structures with high slopes.

6. Conclusions

Based on the presented results, the combination of 2PA-technique and the utilization of positive photoresist demonstrates an alternative method for the LIGA-process. 2PA exist solely in the voxel. Hence, it enables high precision structuring of positive photoresist and the feasibility of maskless, arbitrary fabrication of three-dimensional structures.

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