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Fabrication of high-aspect-ratio sub-diffraction-limit microstructures by two-photon-absorption photopolymerization

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ABSTRACT Micro-cell structures with side-walls as thin as 0.70 μm and aspect ratios as high as 6.7 are fabricated by single-layer writing through two-photon-absorption (TPA) photopolymerization. The use of a moderate-numerical-aperture (N.A.) objective lens to obtain a much more elongated voxel and an in situ ultraviolet (UV) pre-exposure step to improve the sensitivity of TPA photopolymerization are the main factors responsible for the high aspect ratio and sub-diffraction-limit resolution that are achieved.

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1 Introduction

The fabrication of complex three-dimensional (3-D) microstructures by two-photon-absorption (TPA) photopolymerization [1] of photosensitive materials has been demonstrated in recent years. This technique has been widely studied in the fields of micromachines [2–6], photonic devices [7–9], and 3-D optical data storage [10–12]. Using this unique method, one can fabricate objects with sub-diffraction-limit resolution and functional devices such as micro-oscillators [2], microgearwheels [3], light-driven rotors [4], micro-tweezers [5], micro-chains [6], and photonic crystals [7–9]. Compared with other methods of microfabrication, such as optical lithography, electron beam lithography, focused ion-beam etching and laser ablation, it has the advantages of being maskless, single stepped, 3-D, and high resolution.

To achieve TPA photopolymerization in an ultraviolet (UV)-curable resin, intense near-infrared (near-IR) femtosecond (fs) lasers are used as light sources. Usually high-numerical-aperture (N.A.) microscope-objective lenses are employed to focus the fs laser beam tightly into the resin to reach a very high photon densities near the focal spot. Most photopolymerizable resins are composed of UV-activated photoinitiators, oligomers, and monomers. In the single-photon-absorption (SPA) process, the resin is illuminated with a UV light and the photoinitiators absorb UV photons to generate radicals for the subsequent polymerization process. The process can alternatively be initiated by near-IR light via two- or multi-photon absorption under high-intensity illumination. Since SPA is a linear process, polymerization can occur outside the focal region along the light path and, consequently, low spatial resolution in both the lateral and axial directions occurs. In comparison, the photopolymerized volume in the nonlinear TPA process is more confined within the focal region, owing to its quadratic dependence on the optical field intensity. In addition, the intensity threshold effect due to radical scavenging by dissolved oxygen molecules [13] inhibits the initiation and propagation of polymerization unless the exposure energy exceeds a critical value. Owing to the quadratic dependence and the intensity threshold effect, the volume of solidified resin (voxel) can be made smaller than the focal spot with TPA polymerization by properly controlling the laser power and exposure. In addition, its ease of 3-D manipulation is unachievable by conventional lithography techniques. Based on these advantages, one can fabricate complex stereo microstructures with sub-diffraction-limit resolution by scanning the focal spot along a predetermined path through the liquid resin. However, the concomitant low throughput, due to the need for densely packed multi-layer scanning of a sub-micron focal point, greatly limits its utility in real device manufacturing.

In this letter, we demonstrate the fabrication of a high-aspect-ratio sub-diffraction-limit micro-cell structure in high-speed single-layer scans using TPA photopolymerization with an extra step of in situ SPA pre-exposure. By varying the pre-exposure time, we obtain linewidths ranging from 0.28 to 0.70 μm and aspect ratios from 2.9 to 6.7, respectively. The experimental results indicate that the pre-exposure step plays a key role in this manufacturing process.

2 Experiments

The experimental setup is sketched in Fig. 1. We put a drop of commercially available UV-photopoly-

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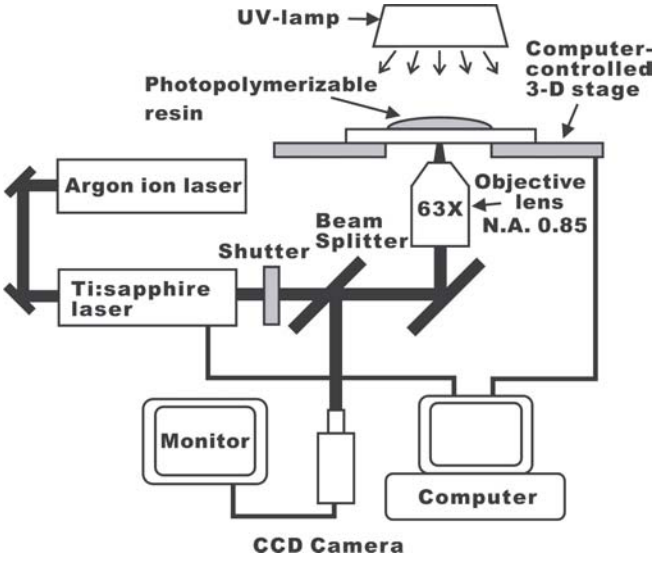

FIGURE 1 Experimental setup. A 4-W UV-lamp is held 3 in above the samples to pre-cure the liquid resin

merizable resin on top of a cover slip. The resin (3D system, SL-5510) is transparent to near-IR light and solidifies when it is irradiated with UV light. A mode-locked Ti : sapphire laser operating at a wavelength of 780 nm generates near-IR light pulses whose pulse width and repetition rate are 45 fs and 86 MHz, respectively. The fs laser pulses are tightly focused onto the liquid resin by a 63× objective lens with a moderate N.A. of 0.85. At the focus, the estimated lateral spot size (diameter) and the confocal parameter are 0.87 μm and 1.51 μm, respectively. The samples are scanned with a computer-controlled piezo-electric 3-D translation stage (Physik Instrumente, P527.3), which moves along the pre-programmed path. To control the exposure time, a computer-controlled mechanical shutter with a 10-ms rise time is used. A beam splitter is placed behind the shutter to image the focused laser spot on the resin–glass interface onto a CCD camera, so as to monitor the vertical displacement of the focal spot.

In our study, we use a single-layer writing method to directly write high-aspect-ratio square micro-cell structures. The micro-cell structure is composed of 36 unit cells. Each unit-cell is 15 μm × 15 μm in dimension. Apart from the regular TPA writing process, we introduce an additional in situ SPA pre-exposure step to improve the overall quality of our micro-cells. This pre-exposure process employs a 4-W UV-lamp held 3 in above the samples to irradiate the liquid resin. To demonstrate the effect of our SPA pre-exposure method, we made a series of the same microcells with various SPA pre-exposure times while keeping the TPA photopolymerization parameters unchanged. For all samples, the incident laser power before entering the cover slip was 8.7 mW and the scanning velocity was 15 μm/s. A complete scan takes less than 3 min. After fabrication, we used acetone to remove the unsolidified resin. Finally, the fabricated structures were examined and measured by an inverted optical microscope (Nikon, TS-200) and a high-resolution scanning electron microscope (SEM) (Hitachi, S-3500 N).

3 Results and discussions

Our in situ SPA pre-exposure method is somewhat different from that proposed by Sun and coworkers [3]. They exposed the liquid resin to a 150-W xenon lamp for 60 s with quick stirring before writing their 3-D micro-gearwheels with TPA photopolymerization. Since UV photons cannot penetrate deep under the surface, vigorous stirring of the resin through the pre-exposure process was needed to ensure uniform pre-polymerization. In our pre-exposure process, the liquid resin drop is thin and stirring is unnecessary. UV exposure creates short-chain photopolymers, which have two effects on the subsequent TPA photopolymerization: First, they enhance the viscosity of the resin and prevent flowing during pattern writing. Second, they reduce the near-IR dose required to reach the solidification threshold. Unlike Sun et al., whose purpose was to increase the viscosity so as to minimize component drift and distortion during their multi-layer fabrication of 3-D structures, we exploit the second effect to achieve high-speed single-layer writing of micro-cells.

The measured linewidths and heights for pre-exposure times varying from 0 to 25 s are illustrated in Fig. 2. The effect of the SPA pre-exposure on the wall height is evident. For pre-exposure times in excess of 30 s, the UV-curable resin completely solidifies by SPA photopolymerization. It has been pointed out in [14] that the substrate truncation effect leads to inconsistencies in or misinterpretation of the longitudinal and

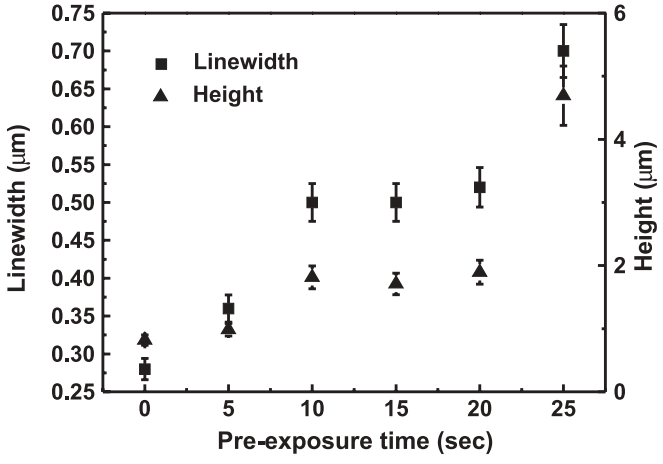

FIGURE 2 The measured linewidths and heights vs in situ UV pre-exposure time in samples made by the single-layer writing method with a fixed TPA dose

transverse voxel dimensions. To avoid this complication, we monitor the vertical position of the laser beam focus, and keep it at the glass–resin interface for all samples. Figure 3 shows SEM images of a sample made by the standard process without UV pre-exposure. Figure 3a and b were taken from the top and at a 75° tilt from the normal direction, respectively. Estimated from these images, the linewidth is about 0.28 μm (or 32% of the laser spot size) and the aspect ratio is about 2.9. The corresponding SEM images of the sample with a 25-s SPA pre-exposure time are shown in Fig. 4 (Fig. 4a and b are taken from the top and at a 75° tilt from the normal direction, respectively.). The thickness of the side-wall is about 0.70 um (or 80% of the diffraction limit), twice as thick as the previous sample, but its height is 5.8 times as high and the aspect ratio increases to 6.7. To the best of our knowledge, this is the first work that uses TPA photopolymerization to successfully fabricate microstructures with a sub-micrometer linewidth and an aspect ratio as high as 6.7 with single-layer writing.

Several groups have reported the fabrication of high-aspect-ratio microstructures in photopolymeric materials. For example, the groups of Horiyama [15] and Wu [16] have made such microstructures by SPA and TPA photopolymerization, respectively. Both of them adopted high-N.A. oil-immersed lenses (N.A. $\approx$ 1.4) as focusing optics and used multi-layer stacking to form high-aspect-ratio structures. In contrast, our method is distinguished from other groups in that the high-aspect-ratio sub-diffraction-limit thin walls are made with single-layer writing. The key strategies to obtain our results are as follows: (1) Instead of the high-N.A. lenses commonly used by other researchers to achieve high resolution, we employ a moderate-N.A. objective lens to obtain a much larger depth of focus (DOF). (Note that the DOF increases as $(\text{N.A.})^{-2}$, while the spot size is only proportional to $(\text{N.A.})^{-1}$.) The effect of the N.A. on the voxel shape can be seen in Fig. 5, which shows the isophotes of the square of the light intensity near the focal region of a Gaussian beam focused by lenses with N.A. = 0.85 and 1.25, respectively. An elongated voxel is obtained with the smaller N.A. lens. (2) The additional in situ SPA pre-exposure step creates short-chain photopolymers in the unsolidified resin, which effectively reduce the required dose for TPA photopolymerization, or equivalently increase the maximum allowable scanning velocity. This feature compensates for the disadvantage of the smaller N.A. objective lens, that is, the lower intensity at the focal region. It is a crucial step for the subsequent pattern writing because, otherwise, the TPA photopolymerization rate would be too low. (3) There is a way to further improve the aspect ratio of the microstructures: since 50% of the voxel is truncated by the glass substrate, one can move the focal point above the glass to minimize the substrate truncation effect and optimize the height of the walls.

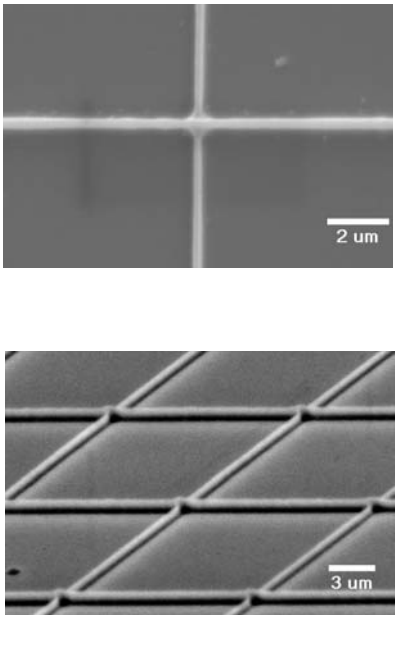

FIGURE 3 SEM images of the micro-cell made by TPA photopolymerization without SPA pre-exposure. **a** and **b** were taken from the top and at a 75° tilt from the normal direction, respectively. Estimated from the images, the linewidth is about 0.28 μm and the aspect ratio is 2.9

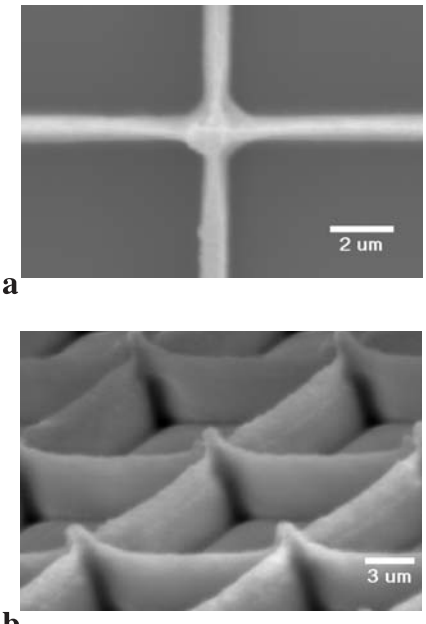

FIGURE 4 SEM images of the micro-cell made by TPA photopolymerization with additional SPA pre-exposure for about 25 s. **a** and **b** were taken from the top and at a 75° tilt from the normal direction, respectively. Estimated from the images, the linewidth is about 0.70 μm and the aspect ratio is 6.7

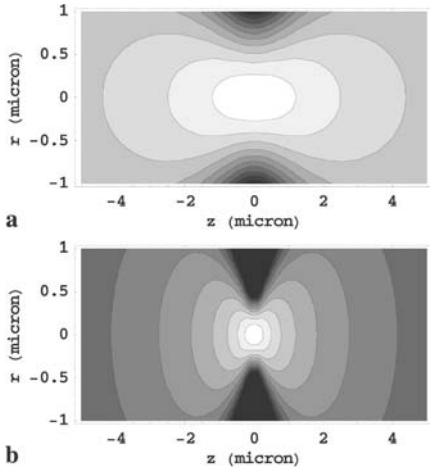

FIGURE 5 Plots of isophotes of the square of the light intensity near the focal region of a Gaussian beam focused by lenses with **a** N.A. = 0.85 and **b** N.A. = 1.25. z and r are the axial and lateral coordinates, respectively. The focal plane is at $z = 0$

4 Conclusion

In summary, we have demonstrated a new approach to fabricating high-aspect-ratio microstructures by TPA photopolymerization. By using a moderate-N.A. objective lens and an in situ UV pre-exposure step, we have successfully fabricated micro-cells with side-walls as thin as 0.7 μm and aspect ratios approaching 7 in high-speed single-layer scans. We believe that this technique can be applied in general to manufacturing high-aspect-ratio objects or devices with sub-diffraction-limit resolution.

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