Three-dimensional microfabrication with two-photon-absorbed photopolymerization

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We propose a method for three-dimensional microfabrication with photopolymerization stimulated by two-photon absorption with a pulsed infrared laser. An experimental system for the microfabrication has been developed with a Ti:sapphire laser whose oscillating wavelength and pulse width are 790 nm and 200 fs, respectively. The usefulness of the proposed method has been verified by fabrication of several kinds of microstructure by use of a resin consisting of photoinitiators, urethane acrylate monomers, and urethane acrylate oligomers. © 1997 Optical Society of America

Recently the microfabrication technology that uses photopolymerization has been intensively studied with a view toward development of new types of micromachines,[1] integrated microfluid sensors,[2] self-organizing light-wave guides,[3] and so on. Applications of technology in micromover systems driven by lasers[4] and in the field of laser trapping[5–7] are also of interest.

Although microfabrication technology with photopolymerization has been used in several fields, the physics of the photopolymerization process in three-dimensional (3D) space is not clear. This means that the spatial resolution attained with photopolymerizing fabrication is uncertain. A theoretical self-consistent analysis of the photopolymerizing materials and the 3D wave field is necessary.

Experimental attempts to improve the 3D spatial resolution associated with photopolymerizing fabrication will also be necessary. Self-organizing phenomena such as self-focusing and self-trapping of a laser beam[3] may be used to improve the 3D spatial resolution.

Because of both the low spatial resolution in the longitudinal direction and the light absorption at nonfocused points with the present method of photopolymerizing fabrication, one must pile up two-dimensional layers to make a 3D structure. This restricts the choice of both the resultant 3D structure of the photosolidification and the practical procedures necessary for the fabrication.

In this Letter we introduce two-photon-absorption[8] into the UV photopolymerizing fabrication process to improve the longitudinal resolution.[9] Two-photon absorption has been applied to fluorescence microscopes, to 3D memory, and to lithography.[8–12] Results of fundamental experiments that verified the possibility of 3D fabrication with two-photon absorption have been demonstrated.[11,12] However, as far as we know, practical micromechanical or optical parts that have structures both in depth and laterally have not been fabricated.

In our method a pulsed near-IR laser is focused inside an UV photopolymerizing material that is photosolidified in only a small volume within the depth of focus because of the squared point-spread function that is associated with two-photon absorption.[9] Moreover, because the resin is transparent to near-IR light, the structures that are in out-of-focus positions do not have much effect on the attenuation of the laser beam. Thus it is not necessary to pile up two-dimensional layers.[1,2]

The UV-photopolymerizable resin that we used consists of a photoinitiator for photopolymerization, urethane acrylate monomer, and urethane acrylate oligomers. The resin is SCR-500 from Japan Synthetic Rubber Company, Ltd.[13] Figure 1 shows schematically the chemical reaction process of the two-photon photopolymerization; I, R, M, Mn, and R–Mn represent photoinitiators, free radicals, monomers–oligomers, polymers, and chained radicals, respectively.

When the near-IR light, which has high peak power, is focused inside the resin, the spatial density of the photons becomes high at the focal point. Each initiator, which usually absorbs a UV photon, absorbs two near-IR photons at the same time and becomes a radical when the spatial density of the near-IR photons is high. The resultant radicals cut the double bonds of carbons in the acrylyl groups in the monomers and oligomers and successively create new radicals at the ends of the monomers and oligomers. The radical combines with another monomer. The process becomes a chain reaction until the chained radical meets another chained radical.

The reaction speed of the above reaction stimulated by the two-photon absorption is proportional to the square of the photon density at each position in the resin, whereas it is proportional to the density itself for a reaction by single-photon absorption. The point-spread function for two-photon absorption photopolymerization would be the square of that for single-photon absorption polymerization.[9] This means that

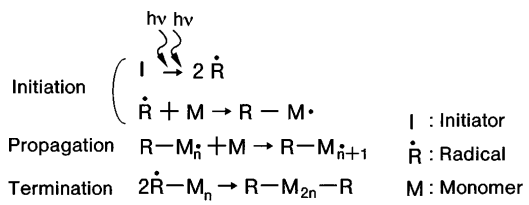

Fig. 1. Photochemical reaction for two-photon microfabrication.

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if we use a pulsed laser of 790-nm wavelength the lateral size of the solidification at the focus would be almost the same as the diffraction-limited light spot at 395 nm and the longitudinal size would be smaller.[9]

Figure 2 shows the optical system that we used for fabricating 3D microstructures with the proposed method. The light source that we used for the two-photon absorption was a mode-locked Ti:sapphire laser whose oscillating wavelength, pulse width, repetition rate, and peak power were 790 nm, 200 fs, 76 MHz, and 50 kW, respectively. The Ti:sapphire laser was excited by an Ar-ion laser of 8-W average power. The beam of the laser was focused into the resin with an objective lens whose N.A. was 0.85. A stage supporting the sample was scanned in three dimensions under computer control. The fabricated structure could be observed from the side of the resin with an objective lens of N.A. 0.4. After fabrication we extracted the resultant structures by removing the unsolidified resin with ethanol.

Figures 3(a) and 3(b) are photographs through unsolidified resin from the bottom and from the side, respectively, of a spiral structure fabricated by the proposed method. The input power of the laser and the total exposure time were 20 mW and 2.3 s and the diameter and the axial pitch of the spiral structure were 6.0 and 10.3 μm, respectively. The width of the spiral wire was nearly 1.3 μm. As far as we know, this is the first attempt to make such a small structure without piling up two-dimensional structures.

Figure 4 shows scanning electron microscopic images of the spiral structure after the unsolidified resin is removed. The input power of the laser and the total exposure time were 34 mW and 1.4 s, respectively. The spiral structure is coated with thin gold film 40 nm thick. The diameter of the spiral structure is 7 μm.

The structures in the deep region are fabricated without being disturbed by those in shallow region. This is so because the near-IR laser is not absorbed by the resin and the difference in refractive index between polymerized and unpolymerized resins is small. The length of the 3D structure fabricated by this method is limited by the spherical aberration rather than by absorption or diffraction of light. If we use the single-photon process, the laser beam much attenuated and the wave front is distorted.

The minimum average power needed by the laser to harden the resin was 20 mW with an exposure time of 8 ms. The minimum exposure is estimated to be 18 J/μm^2 at the focal point. The absorption coefficient for the two-photon process was 0.04% of that for the single-photon process.

The spatial resolution of the proposed method is limited by the radical diffusion and growth of polymer chains outside the illuminated region. However, the effect is smaller than in the conventional single-photon absorption process[1–3] because in the two-photon process the resin polymerizes only in the focused region of high optical density. As a result, the resin does not polymerize beyond the region illuminated by the diffracted laser beam, whose optical density is not high enough to harden the resin.

The next issue that needs to be addressed is use of the proposed fabrication technique to make a probe for laser trapping and a micromover. In addition, a theoretical analysis of the 3D photopolymerization process with both single-photon and two-photon absorption is

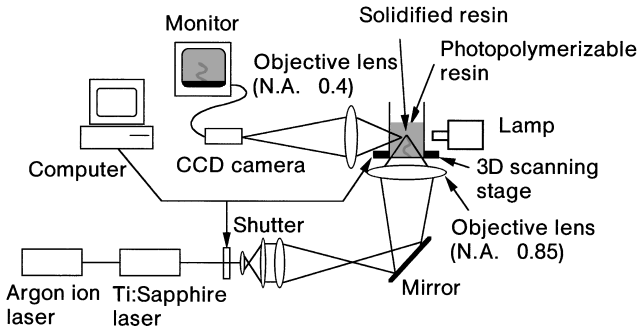

Fig. 2. Optical system for two-photon microfabrication.

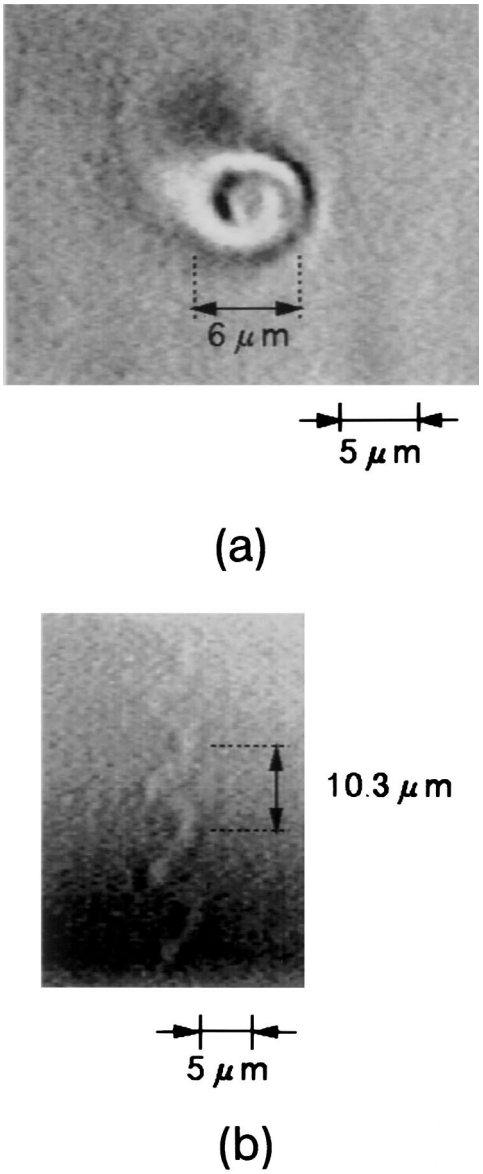

Fig. 3. Microscopic images of a spiral structure made by two-photon microfabrication in unsolidified resin: (a) bottom view, (b) side view.

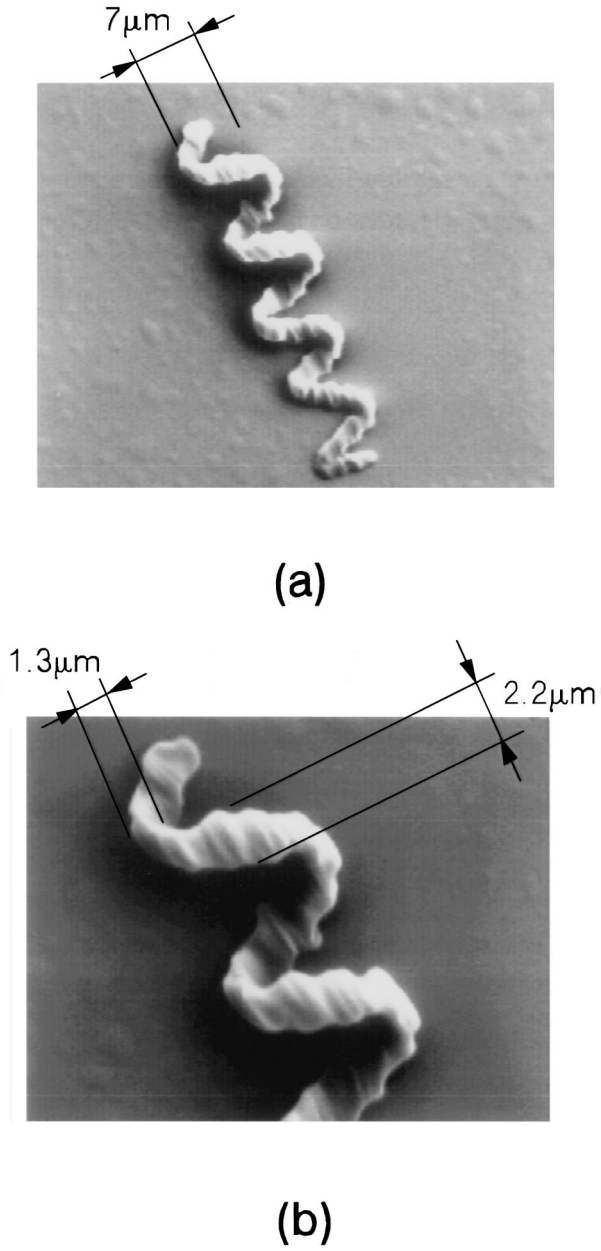

Fig. 4. Scanning electron microscopic image of a spiral structure made by two-photon microfabrication after removal of the unsolidified resin: (a) view of the entire structure, (b) magnified view.

necessary as the basis of microfabrication with photopolymerization.[3]

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