Two-Photon Photopolymerization of Functional Micro-Devices

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The current trend in two-photon laser micro-nano fabrication is device functionalization. In this paper, we report two kinds of functional devices, i.e., optically active microstructures produced by dye-doping photopolymerization and mechanically workable micro-oscillators driven by the laser trapping force. These works would open the door to two-photon production of various practical three-dimensional polymer optoelectronic/photonic devices and microelectromechanical system (MEMS).

Keywords: Two-photon photopolymerization, three-dimensional micro-nano fabrication, Optical MEMS, Femtosecond laser

1. Introduction

Since the first proposal [1], two-photon photopolymerization technology has attracted a lot of research efforts because it is currently the only technique that has intrinsic three-dimensional (3D) fabrication capability. Comparing with conventional lithographies either by ultraviolet (UV) light or by electron beam or x-ray, two-photon photopolymerization has additional merits including (i) ease of structure design and realization. Various complex structures could be produced in one-run operation. (ii) Low requirements to the fabrication system. No vacuum condition is necessary. One major concern to the technology is the spatial resolution issue. That is, in a far-field optical system the fabrication accuracy is always limited by the diffraction limit. To solve this problem, we proposed a sub-diffraction limit (SDL) fabrication method [2, 3]. The basic idea is, optically we tightly focused the laser beam with a high NA (numerical aperture) lens, and chemically we confined the near-focal volume, where desired photochemical reactions occurred, by the radical quenching effect. As a result, a lateral spatial resolution as small as 90 nm has been achieved. Such accuracy would suffice the requirement of most practical photonic/ optoelectronic devices and MEMS. For example, 3D photonic crystals (PhCs) [4-6] working at the communication wavelength of 1.55 µm need a rod diameter (log-pile structure) around 300 nm, which would be easily fabricated with the 90-nm spatial resolution.

A new challenge in the field is device functionalization. The technical progress has provided the possibility to tailor micro-nano devices that function. However, related work hasn’t yet been done. In this paper, we report two kinds of functional devices. First by two-photon photopolymerization of fluorescent dye-doped resin, a 3D micro cage, a micro-gearwheel and a micro-icosahedron have been produced. These are preliminary fluorescence functional devices [7]. Second, by using the SDL technology, we fabricated micro-oscillators with a 150-nm spring radius and drove them by laser trapping [2, 8]. These are functional micro-mechanical devices.

2. Experimental Configuration

The principle of micro-nano fabrication via two photon absorption (TPA) photopolymerization is tightly focusing femtosecond (fs) laser into a photopolymerizable resin and directly writing 3D patterns by scanning the laser focus or sample stage. Due to the quadratic dependence of TPA rate on the laser pulse energy, photopolymerization occurs only at the close vicinity of the focal spot. Then following the scanning locus, a solidified skeleton will be formed, which remains after the removal of unsolidified liquid resin [9, 10].

The two-photon fabrication system was similar to that previously used. The exposure source employed was a 780 nm mode-locked Ti: Sapphire laser, capable of producing laser pulses of ~ 150 fs at a repetition rate of 76 MHz. It was focused into the resin by a high NA (~1.4, oil immersion)
objective lens. Under this focusing condition, the laser beam delivers a transient peak power of 20 GW/cm², or a photon flux density of $8 \times 10^{20}$ photon/(s•µm²). The average power is $10^3$ smaller than that necessary for cw laser to reach the same excitation level. It is due to the strong compressing of laser pulses in both time and spatial domains that TPA was enabled.

(a) 

BDMB

CH$_2$CH$_3$)

O

N

C

C

N(CH$_3$)$_2$

HCAP

(b)

\[ \text{Intensity (a.u.)} \]

\[ \text{Wavelength (nm)} \]

474 nm

Resin

Dye

TPA

Fig. 1. Photopolymerizable resin. (a) Initiators contained, and (b) absorption spectrum of the resin. The emission spectrum of the doped dye is also shown [Refer to Fig. 2].

The resin we used consisted of urethane acrylate oligomers with different molecular weight 480 and 1200, urethane acrylate monomer as a dilutor. The initiators are typical kinds of benzoyl chromophor [Fig. 1(a)], which undergo a α cleavage (or Norrish I photoscission process) at C-C bond upon absorbing photon energy by TPA. The absorption spectrum of the resin is shown in Fig. 1 (b).

3 Optically Functional Devices

Two-photon photopolymerization has not only lateral, but also longitudinal spatial resolution, which is therefore suitable for fabricating 3D devices and integrated systems. Apparently more work should be done on device structure design to fully utilize the fabrication capability. One example that requires 3D features and has already been benefited from the two-photon processing technique is PhC, a composite dielectric structure possessing periodic refractive index distribution. Up to now, PhCs with pronounced photonic bandgap effect [4], and with high-Q defect cavity modes [6] have been produced by the two-photon photopolymerization technology. If fluorescent active media are combined with PhC structures, high-efficiency optoelectronic devices such as laser diodes or amplifiers would be enabled.

A simple way to induce fluorescent property into PhCs is directly doping fluorescent dye into photopolymers. To reach this end, we used a laser dye, LD490 (Exciton Inc.), of which the major component is Rhodamine B. Its absorption and emission wavelengths are located at 396 nm and 474 nm, respectively, as shown in Fig. 1 (b). The resin was dissolved to ethanol solution of LD490 till saturation, and then the doped resin was directly utilized for microfabrication.

Fig. 2. A 3D micro-cage and its fluorescent images obtained at cross-sections of different heights.

The fluorescence wavelength of the dye was overlapped with absorption curve of the resin. Hence, the fluorescence arising from two-photon excitation of the dye can also cause photopolymerization, which may degrade the fabrication spatial resolution. This problem was
solved by optimizing the fabrication laser pulse energy and the concentration of Rhodamine B, so that local radical concentrations initiated by the TPA fluorescence was lower than the TPA polymerization threshold, where radicals were quenched by, e.g., dissolved oxygen. Judging from experimental results, spatial resolutions were not degraded till Rhodamine B concentration of $1.0 \times 10^{-4}$ M.

Figure 2 shows fluorescence images of a $5.4 \mu m \times 5.4 \mu m \times 5.4 \mu m$ cubic cage made of the doped resin. The images were obtained by two-photon confocal scanning the cage at different height levels. The fluorescence intensity was found much stronger than that necessary for reading, showing that not only the dye was incorporated, but also its fluorescence attributes were preserved.

The image in Fig. 2 was obtained by two-dimensional (2D) optical cross sectioning. If series of 2D images sampled from the entire object are given, a 3D fluorescence image of the object could be reconstructed. Shown in Fig. 3 are thus obtained micro-icosahedron [Fig. 3 (a)] and micro-gearwheel [Fig. 3(b)] images.

The preservation of high spatial resolution after dye doping into resin, and preservation of the fluorescence activity of the dye after a strong laser irradiation, show a promising prospect to apply the dye doped resin for producing PhC-based optoelectronic devices, which would be the immediate task of our future research.

4. Mechanically Functional Devices

Functional MEMS is another topic of our research. As the first step in this direction, we tried micromechanical devices. Fig. 4 shows springs with a cord radius of 150 nm, and the spiral pitch and diameter are both $2 \mu m$.

![Image of micromechanical devices](image)

It is noteworthy that the cord diameter of the spring is far less than the fabrication wavelength of 780 nm. Mechanically motivating a spring of such a small size is technically challenging. To solve this problem, we fabricated micro-oscillators that included the micro-spring, as shown in Fig. 5, and drove them by the laser trapping force [11-13]. The spring in (a) is attached to an anchor at one end, and at the free end a micro-bead was polymerized for facilitating the laser trapping. In (b), a bead was linked by two springs. If the beads were trapped by a focused laser, they would follow the movement of the focal spot, by which, the springs can be prolonged, compressed, and bent. To simplify analysis, we choose the single spring system [Fig. 5 (a)].

The anchor has a side length of $8 \mu m$. The bead, located 10 $\mu m$ above the substrate, has a diameter of $3 \mu m$. Figure 5 (a) is an in-situ photo microscopic image of the fabricated oscillator system (before removing unsolidified liquid resin). The spring and the bead should not adhere
to the substrate so that a free movement is possible. This was evidenced by Fig. 6, which was recorded when slightly shaking the sample cell and therefore the bead flowed with the liquid.

The oscillator system was kept in the developer of ethanol so that the buoyancy would partly balance the gravity to reduce the bead-substrate friction. The same laser system as that utilized for TPA photopolymerization, but a wavelength tuned to 820 nm, was used for the laser trapping. The laser has an average power of 19 mW, which may induce a lateral trapping force of not less than 3 pN, corresponding to 20 times of the bead gravity.

Experimentally it was clearly observed that the bead was three-dimensionally trapped in the focus of laser, and could be arbitrarily manipulated. When released from a prolonged state by stopping the irradiation, an oscillation was initiated. However, due to the extremely small size of the device, the viscosity of liquid plays a critical role in determining oscillation modes. In the current study, the oscillation was observed to be a highly damped one. By fitting the displacement-versus-time curves to the oscillation equation using the least square method, the spring constant of the oscillator was deduced to approximately 8.0 nN/m.

In conclusion, we have succeeded in fabricating optically and mechanically functional micro-devices by using two-photon photopolymerization technology. As a natural extension of the current research, future work will be focused on polymer optoelectronic devices and functional MEMS.

References