Microfabrication of Two and Three Dimensional Structures by Two-Photon Polymerization

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Femtosecond infrared laser pulses are useful for laser micro/nanofabrication of two and three dimensional (2D & 3D) structures through multiphoton process. Two-photon polymerization were used for fabricating 2D & 3D polymeric structures by several methods. These features were produced by multibeam interference and direct writing techniques. These methods provide simple and rapid approaches for creating templates with designed 2D & 3D structure in micro/nanometer scales. A new method to introduce metal oxides nanoparticles into the 3D polymeric structures also has been proposed and developed for fabricating 3D structure of polymer nanocomposites. This new method has been expecting to be applied for fabrication of functional 3D micro/nano-mechanical machines (M/NEMS) and micro/nano-devices.

Keywords: two-photon polymerization, two and three dimensional structures, microfabrication

1. Introduction

The nonlinear, multiphoton process of two-photon absorption (TPA) has been gaining greater interest among a number of multidisciplinary areas, particularly in the rapidly developing fields of multiphoton fluorescence imaging, optical data storage and switching, optical sensor protection, telecommunication, three-dimensional (3D) microfabrication and photodynamic therapy (PDT) [1-3]. Two-photon polymerization, which is initiated by TPA of photo-initiator, is a potentially useful tool for the fabrication of polymeric two and three-dimensional (2D & 3D) structures, which have been expecting to be used as micro/nanoscale devices and systems, by using femtosecond infrared laser without photo-masks. Comparing with micro-particle self-organization, lithography and various chemical etchings, two-photon polymerization [4-8] as a novel photochemical scheme proposed by some of the current authors, has exhibited unique

advantages for micro/nanofabrication in its intrinsic 3D processing capability and flexibility in using versatile functional polymer materials. 3D micro/nanostructures including log-pile photonic crystals (PhCs) with strong bandgap effects [5], rotatable gearwheels, a 8- μ m-long micro-bull and a 300-nm-diameter workable oscillator [6,7] by direct laser writing, and PhCs by rapid multibeam interferential patterning [8] have been readily produced. Recently, 3D diamond photonic crystal structure, which is one of the most complicated 3D structures, has successfully fabricated by two-photon polymerization [9]. These results give us good samples those demonstrated the capability of two-photon polymerization for fabricating micro/nano-mechanical machines system (M/NEMS) or micro/nano-devices under micro/nano-meter scale and in 3D.

However, for giving those M/NEMS and micro/nano-devices different functions, it is

necessary to develop new polymeric materials, which have novel functional properties. One way for introducing photonic and electronic functions into polymeric materials is doping nanoparticles. The nanoparticles of noble metals and metallic oxides are interesting species because when size is downscaled to nanometers order, materials demonstrate novel optical, electronic, magnetic, and mechanical properties, which is the major motivation of the current intense research on nanoparticles. Thus, 2D & 3D structures of polymer/metallic oxides nanoparticles composite materials could be expected to play an important role in functional micro/nanodevices for future applications. However, dispersing nanoparticles into photopolymerizable resin is difficult, because of the high viscosity of photopolymerizable resin.

Here, we review several methods for fabrication of 2D & 3D polymeric structures by two-photon polymerization, and show a new method to introduce metal oxide nanoparticles into 3D polymeric structure [10].

2. Structures Fabricated by Multibeam Interference

2.1 Two Dimensional (2D) Rod Array

Multibeam interference is a suitable technique for fabrication of periodic structures. Although the technology was first applied to create 3D structures [6], it also be practically useful for preparation of 2D lattices, for example, as compact active or passive planar waveguides of forthcoming integrated optical circuits.

Photopolymerisable urethane acrylate with benzoyl photoinitiator, a commercial resin SCR 500 provided from JSR, was used in our experiments. The resin was dropped on a slide glass and spin-coated for making a film sample with thickness of several micrometers. Another slide glass was covered on the sample for determining the thickness of resin layer and preventing photo-generated radicals from quenching by oxygen in ambient air.

A 780-nm, 80-fs, 82 MHz Ti: Sapphire laser was used for two-photon polymerization. The beam of laser was split into 4 beams with a diffractive beam splitter and then the beams were focused into the sample. Laser pulses from 4 beams underwent no phase shift with each other and overlapped in both spatial and time domains, producing a stable square distribution of rod-like first-order maximums of light intensity. By carefully controlling the laser intensity, I , exposure time, t ,

Figure 1. SEM images of two-photon 4-beam interferential polymerization-induced 2D rod array or PhCs.

polymerization of urethane acrylate occurred only at these high intensity volumes. After finishing exposure, the unpolymerized resin was removed by ethanol.

Fig. 1 shows SEM images of two-photon polymerized 2D rod array. The rods with length of $3\text{-}\mu\text{m}$ have a mean diameters of $F = 0.9\text{ }\mu\text{m}$ with top-bottom difference of less than 4%. The rod thickness was determined by both of exposure time (t) and laser intensity (I). For example, the two-photon photopolymerization thresholds of the resin were estimated to $I_{th} = 90\text{ mW}$ at each beam for $t = 1\text{ s}$, and $t_{th} = 2\text{ s}$ for $I = 60\text{ mW}$. The 2D rod array in Fig. 1 was created by 60-mW/cm^2 5-s exposure, followed with 2-hour post-developing at room temperature. Such perfect 2D polymer photonic lattices as shown in Fig. 2, not possible to produce by conventional technologies like chemical etching or project- and soft-lithography, give a new application example of the powerful laser photopolymerization micro/nano-fabrication method.

1.2 Three Dimensional (3D) Network

Post-developing process also plays an important role in fabricating the features of polymeric structures. Using the identical exposure, but varying post-developing duration led to dramatic change of resultant solid patterns. Fig. 2 shows a SEM image of a network which was created by a 60-min post-developing process. In the case, not only the 2D rod array but also fibers vertically connected between the nearest neighboring rods were observed. The fiber diameter ranges from 50 nm to 80nm, just one tenth of the rod diameter, F . Experimentally it was found that by using oxygen

Figure 2. SEM images of two-photon 4-beam interferential polymerization-induced rod-arraybased nano-network.

quenching effect it is possible to reduce F beyond the optical diffraction limit of 460-nm, till 300 nm, which is still much larger than the fiber thickness.

For confirming the effect of post-developing process, we varied post-developing duration and took the images with different post-developing times, as shown in Fig. 3. The formation and growth of cylinder holes were confirmed, and the generating process of 3D network could be explained as follows [11].

First, the cylinder holes appeared even after short post-developing time due to solubilization of urethane acrylate monomers, which had not been polymerized. However, this process is confusable and self-sustaining, it leads the holes appearing randomly at the first stage of post-developing process.

With increasing post-developing time, the thin boarding walls of roughly 100-nm thickness appeared. Considering a horizontal cross-sectional plane of the interferential pattern, the light intensity, although steeply distributed, but is continuously spread from bright to dark spots. It may lead polymerization not only occurring at the entire interferential volume. Therefore, there is not clear-cut boundary between the polymerized and less polymerized region. In the region between two bright spots, polymerization velocity should be slow, it created only polymers with low polymerization degree were generated. Those polymers should show a lower solution velocity than unpolymerized monomers. This difference of solution velocities between those polymers with low polymerization degree and unpolymerized monomers leads to a self-organization of polymers in the dissolving process. Finally, the 3D nano-network, which consisted of 2D rod array and

Figure 3. Hole formation at the initial stage of post-developing process (left), and inter-rod film appearance of thin boarding wall when dissolving proceeded.

nano-fibers, was formed.

3. Three Dimensional (3D) Structures Fabricated by Direct Laser Writing Technique

3.1 Three Dimensional Diamond Structure

Direct laser writing technique is powerful for 3D fabrication of micro/nano-scale devices. For using direct laser writing technique, an 80-fs-pulsewidth and 780-nm-wavelength femtosecond laser that was mode locked at 82-MHz-repetition rate was employed as the two-photon irradiation source. The laser beam was focused by a high numerical aperture ($NA \sim 1.4$) oil immersion objective lens.

In order to maximize photonic bandgap effect, we selected a covalent-bond type diamond crystal structure consisting of atoms and bonded rods as our target. Fabrication data file was generated by CAD (computer-aided design) software. Sample scanning, relative to the focal spot, was realized by a 3D piezostage translator with an accuracy of less than 1 nm. The photopolymerisable resin, SCR 500, as mentioned before, was used to fabricate a 3D photonic crystal structure. Fig. 4 shows a $\langle 100 \rangle$ -orientated $8 \times 8 \times 2$ -period crystal fabricated by the pure resin, where the lattice constant is $2.5 \mu\text{m}$, meaning that the nearest atom distance of $1.1 \mu\text{m}$. The diameters of bonded rods and photonic atoms were $500 \mu\text{m}$ and $580 \mu\text{m}$, respectively. The structure was magnified under SEM and shown as inset of Fig. 4, from which a quite smooth rod surface was observed.

3.2 Three Dimensional Structure of Nanocomposite

Meantime, we also used another modified resin for improving refractive index of polymer. Titanium (IV) ions were induced into SCR 500 by mixing titanium (IV) complex solution with the resin. To prevent the reaction between titanium (IV)

Figure 4. Two-photon photopolymerized diamond PhCs. The shadowed parts are shown by the top left-hand side inset.

Figure 5. Micro-sized three dimensional periodic structure of inorganic nanoparticles-polymer composite materials produced by two-photon polymerization and post chemical reactions.

ions in resin and water molecules, this sample was kept between two cover slides. After finishing fabrication, the sample was inserted in methanol and two cover slides were separated. When the sample was put in air, the titanium (IV) ions reacted with water containing in air. At that time, titanium oxide (TiO_2) nanoparticles were generated partly at the polymeric micro/nanostructure. With 2 hours of thermal treatment at 250°C , more TiO_2 nanoparticles were precipitated in polymer. Therefore, a micro/nano-scale structure of composite materials of polymer and inorganic nanoparticles was fabricated by two-photon polymerization and post-chemical reactions. By using different functional materials, it should be possible to give micro/nanostructures, i.e., nanodivices and nanomachines, unique properties, which could be expected for various applications. quite smooth rod surface was observed. However, when the resin contained titanium (IV) ions was used, we observed the nanoparticles on the surface of polymeric structure as shown in Fig. 5. It shows the clear evidence that the nanoparticles of titanium oxide were generated in polymer after two-photon polymerization.

4. Summary

We have successfully demonstrated micro/nanofabrication of different 2D & 3D structures by two-photon polymerization. The laser nanofabrication technology for 2D & 3D structures could be used for producing optoelectronic devices and integrated systems with functional polymer and composite materials.

Acknowledgments

This work has been supported by Nonlinear Nanophotonics Project, CREST program, Japan Science and Technology Agency (JST).

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