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Control of multiphoton process within diffraction limit space in polymer microstructures

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Abstract

Femtosecond laser pulses were used for laser fabrication using two-photon-absorption. By imaging microstructures during laser fabrication, we precisely controlled the sizes and positions of optical functions in the microstructures. We fabricated a two-dimensional periodic array of polymer microstructures using two-photon-induced photopolymerization, and developed a technique of recording optical data with a spatial resolution of less than 1 μm in three-dimensions. This optical recording was achieved by using a femtosecond laser with near-infrared wavelength to induce two-photon photodegradation of fluorescent chromophores.

Keywords: Two-photon-induced photopolymerization; Polymer microstructure; Dendrimer; Fluorescent bits

1. Introduction

Pulse lasers have been used for many years for many different purposes ranging from machining to scientific applications [1]. Typical pulse durations range from a few milliseconds to a few nanoseconds. New laser technologies have pulse durations down of a few femtoseconds. This enabled the discovery of a type of light–matter interaction. This shows that femtosecond laser technology has opened the door to a wide range of applications and overcome the drawbacks of conventional laser applications. The most promising technology using the short-pulse laser beam is material processing using multiphoton absorptions [2–6]. The short pulse duration allows power densities above the multiphoton absorption threshold. Furthermore, this laser processing is capable of very high spatial resolution with the highest precision as fine as the range of hundreds of nanometers. In combination with the multiphoton absorption process, photopolymerization using a femtosecond pulse laser has been explored to fabricate three-dimensional submicrometer structures. This multiphoton-induced photopolymerization can be applied not only to the three-dimensional devices, but also to optical memory storage devices with high data density [7]. Advantages can be achieved by focusing laser beams to within 1 μm of a target, where the multiphoton process occurs within the diffraction limit of the light.

Polymers and organic materials in the field of laser fabrication are considered to be promising because of their flexible properties in the optical region from UV to near-infrared wavelengths. Consequently, current efforts to fabricate miniature structures are geared toward polymer optical devices. Several three-dimensional polymeric structures have been shown to have photonic band gap structures, waveguide structures, and microchannel structures [8–11]. For subsequent applications, pointed-defects in the photonic band gap materials have been fabricated at the desired position for advanced photonic devices. The technique is based on photon-mode recording, which can be achieved by causing a photochemical reaction within the medium. In photon-mode recording, light characteristics such as wavelength, polarization, and phase can be multiplexed to enable data storage, and thus have the potential to dramatically increase the possible optical functions.

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We previously investigated a polymer material for use as an optical high-gain medium and showed that a distributed-feedback structure enabled laser emission. The observed optical responses were attributed to the precise control of the polymerized periodic structure fabricated through the two-photon-induced (TPI) laser lithography [12,13].

Therefore, the technology can be extended to prepare an optically active microstructure, if the fabrication can be controlled and the structure analyzed with submicrometer resolution at the same time. In this study, we developed a method that uses confocal optical imaging to overcome the current limit of fabricating microstructures by introducing additional optical information on optical defects. Optical instrumentation for the confocal imaging is used in addition to that of the femtosecond laser beam for the two-photon-absorption. Thus, we were able to modify the microstructure at precise positions, including inside the medium, in three-dimensions.

2. Experiment

The photocurable resin used for the TPI polymerization consisted of acrylate pre-polymer, TBT, and 4,4′-bis(*N*,*N*-dimethylamino)benzophenone (DABA) at a mixing ratio of 75:25:0.5. TBT is a cross-linkable binder, and DABA is a radical photoinitiator. A DCM-doped dendrimer was mixed with the resin at a ratio of 1:9 to introduce the fluorescence into the microstructure. The advantages of using dendrimer have already been discussed elsewhere [12,13]. The TPI polymerization was performed in a sandwiched-glass cell with a cell gap of 7.5 μm. A beam from a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics, 700–780 nm, pulse width <130 fs, repetition rate=80 MHz) was directed at an objective lens and then focused on the resin. A 100× objective lens with a numerical aperture of 0.95 was used. The average beam power in the resin was less than 10 mW. At this power, no thermal damage was observed in the polymerized structure. The two-photon-absorption of DABA molecule was maximized at 670 nm and tailed off around 760 nm. Exciting the DABA molecule using the pulse laser at 700 nm can initialize the TPI photopolymerization. DCM has its maximum absorption at 479 nm. Therefore, the resin transmits the light at 700 nm, and is hardly polymerized due to one-photon absorption. X-, y-, and z-stage scanners were moved along a laser-focused point to fabricate three-dimensional polymeric structures. The scan rate of 50 μm/s was kept constant during the experiments. A reflection confocal microscope was located on the scanners, and was used to analyze the polymerized microstructure. The laser beam at 488 nm was used to analyze the fluorescence from the sample in the confocal optical geometry to obtain the two- or three-dimensional optical images.

3. Results and discussion

Optical microscope images of the polymer microstructures of periodic dots with triangle lattice constants between 2.0 and 0.6 μm are shown in Fig. 1. The microstructure was fabricated by moving the resin in the *x*, *y*, and *z* directions relative to the focus point of the femtosecond laser beam. The contrast in the optical image was caused by a change in the refractive index when a region changed from unpolymerized to polymerized. Under laser excitation, the photopolymerization was initiated by a radical mechanism following an excitation of a photoinitiator caused by two-photon-absorption. Because the rate of absorbing two photons simultaneously has a highly nonlinear dependence on laser power density, the two-photon-absorption process is highly localized in the vicinity of the focal point of a laser beam. This property can even result in the resolution of TPI polymerization that is below the diffraction limit of the illuminated laser light. The diameters of the micro-rods shown in Fig. 1a–d significantly depended on the laser intensities from the mode-locked Ti:sapphire laser. The diameter of the micro-rods varied from about 0.5 to 1.0 μm was changed as the laser intensities. The threshold of laser intensity for TPI polymerization was about 4.5 mW; at such laser intensity, polymerized rods could not stand alone, as shown in Fig. 1d. Since the TPI photopolymerization took place within the size of the diffraction limit of used laser light, the lattice constant of the triangle was reduced to

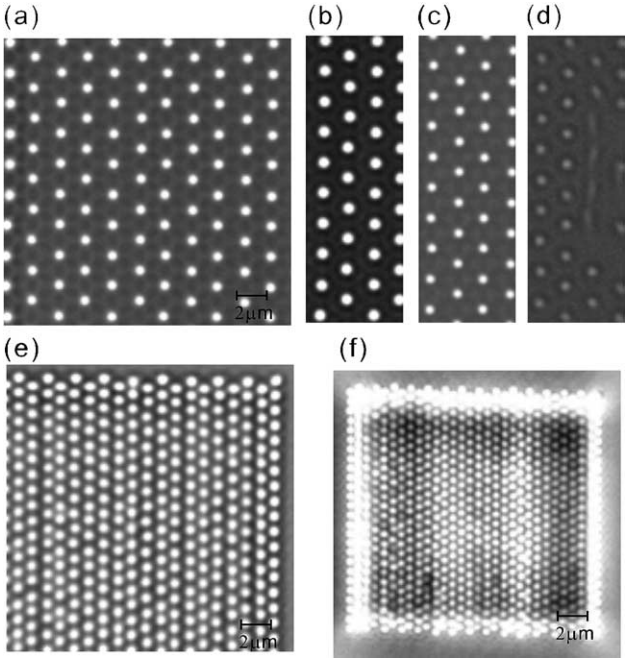

Fig. 1. Optical microscope image of polymerized microstructure made using TPI polymerization technique. Laser intensities for TPI polymerizations were (a) 7 mW, (b) 6 mW, (c) 5 mW, and (d) 4 mW. Lattice constants of triangle structure were (a–d) 2.0 μm, (e) 1.0 μm, and (f) 0.6 μm. Because of resolution limit of optical microscope, images e and f were measured in dark-field mode.