Fabrication of Periodic 3D Nanostructuration for Optical Surfaces by Holographic Two-Photon-Polymerization

Yi-Hsiung Lee, Yi-Jui Liu, Patrice L. Baldeck, and Chih-Lang Lin

***Abstract*—This study fabricated periodic 3D nanostructures by using a periodic voxel array for light extraction. Two-photon polymerization (TPP) is a well-known technology used for generating complex 3D micro- and nanostructures with sub-100-nm resolution. Because of the periodic voxel-by-voxel array fabrication process, the fabrication of holographic two-photon polymerization (HTPP) can be faster than that of traditional TPP. HTPP promises a flexible technique to fabricate an arbitrary periodic 3D structured optical surface. In this research, we used a 25 × 25 beam-splitting holographic mask to generate a periodic focus in a photocured material and to systematically fabricate complex 3D nanostructures at rates of mm ²per minute. The optical responses of nanostructures with a 1 μm period fabricated in a polymer were characterized using 3D optical microscopy. The experimental results of the light distribution demonstrated favorable agreement with those of the simulation. In the light-extracting experiment, the light extraction capability of the gold-layer nanostructures was 3.6 times higher than that of the glass without nanostructures.**

***Index Terms*—Two-photon polymerization, HTPP, nanostructures, electroless gold plating, light distribution, light extraction.**

I. Introduction

In the past decade, periodic polymer nanostructures have been extensively used in light applications such as optical data storage [1], fiber optics [2], and photonic crystals [3]. Periodic polymer nanostructures can be generated using rolling-mask lithography [4], laser interference lithography [5], and laser direct writing [6]. Laser-direct writing can be used to fabricate arbitrary 3D micro- and nanostructures easily by applying two principles: subtraction-type and addition-type [7]. Subtraction-type laser direct writing, Cheng *et al*. [8] employed femtosecond laser to directly generate micro- and nanostructures onto the ITO surface of LEDs but generated debris and thermal damage. Addition-type laser direct writing, also called two-photon polymerization (TPP) fabrication, is the potential technology for fabricating an arbitrary 3D nanostructure, which is integrated with many voxels [9], [10]. A voxel is generated in regions in which the laser energy is higher than the threshold energy by using an objective lens in a photocured material without debris and thermal damage [11].

TPP technology has several advantages, such as no need for a special operating environment, a sub-100-nm resolution, and simple fabrication of a 3D complex structure by using diverse types of photocured materials. Conventional TPP manufacturing is not effective in fabricating high-porosity or thin structures at fabrication rates ranging from mm ²to cm ², because of voxel-by-voxel fabrication processing. Therefore, to shorten the processing time, a TPP system can be integrated with particular instruments such as microlenses [12], scanners [13], and holographic masks [14]. Holographic two-photon polymerization (HTPP) fabrication is a common method that involves using a holographic mask to separate a single beam to multiple foci. In the fabrication methods, multiple foci are periodically fabricated along voxels arranged in a parallel configuration in a photocured material. The processing time is shortened because of the parallel configuration of the voxels, which enable a simultaneous voxel-by-voxel processing. In other words, HTPP promises a flexible technique to fabricate arbitrary periodic 3D micro/nanostructure by means of point-by-point processing.

In this study, we employed HTPP to fabricate a 3D structured optical surface. We used a 25 × 25 beam-splitting hologram with a TPP system to simultaneously fabricate arbitrary periodic 3D nanostructures at a rate of mm ² per minute. Periodic polymer nanostructures were used for light distribution experiments and periodic polymer nanostructures with gold layers were used for light extraction experiments.

II. Experiment Methods

A. Design

For enhancing light exaction, we sought to design a structure that can be integrated with five voxels (Fig. 1(a)). A single nanostructure was integrated with five voxels: The base layer was integrated with four voxels and the second layer was integrated with a single voxel. The distance between voxels was 170 nm in the x- or y direction, and the layer thickness was 600 nm in the z direction. Fig. 1(b) shows a 25 × 25 array of the integrated voxels. The pitch between nanostructures was 1000 nm.

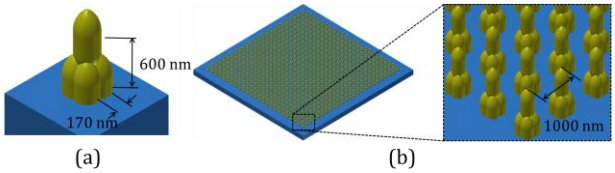

Fig. 1. (a) Dimension of a nanostructure, and (b) dimension of 25 ×25 nanostructures and their details.

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B. Instruments

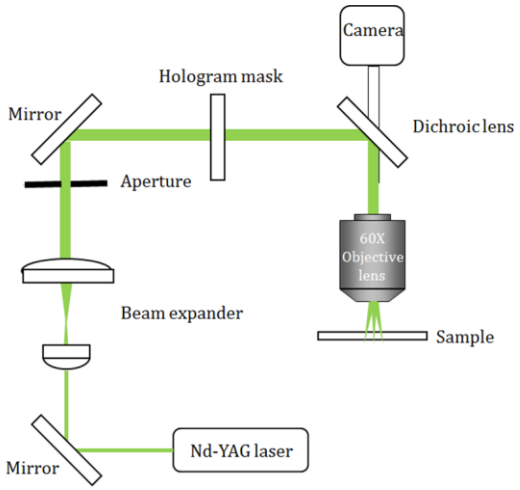

Fig. 2. HTPP setup.

As shown in Fig. 2, the fabrication was performed using 1-ns pulses from an amplified self-Q-switched Nd-YAG laser with a second-harmonic wavelength at 532 nm, a repetition rate of 135 kHz, and an average power of 358 mW (each beamlet was 0.57 mW). The expanded laser beam was phase-modulated by a transmission hologram immediately before focalization in a 25 × 25 array of foci by using a 60x oil-immersion objective lens with a numerical aperture of 1.45. Arbitrary 3D nanostructures can be produced by moving the XYZ piezo stage according to computer-aided design trajectories. For HTPP fabrication, the photocured material used was PEGDA, and the reflective index was 1.47 according to the SIGMA company datasheet. After HTPP fabrication, the sample was immersed in 4-methy1-2-pentanone for 5 min and acetone for 5 min, and was subsequently dried for the light distribution experiment. For the light extracting experiment, we immersed the sample in a 20% v/v solution of ethylenediamine in absolute ethanol for 5 min before drying and immersing the sample in absolute ethanol for 10 min and deionized (DI) water for 10 min. The sample was then immersed in a 0.1% wt $HAuCl_4$ aqueous solution for 20 min and DI water for 10 min, and was subsequently dried for obtaining periodic nanostructures with gold layers.

C. Fabrications

For nanostructure fabrication, we integrated a holographic mask with the TPP system to separate 25 × 25 multiple foci from a laser beam on the image plane of the 60x oil-objective lens; thus, we could fabricate 625 voxels simultaneously in the photocured material. The distance between voxels was 1000 nm because the distance between laser foci was 1000 nm. In HTPP fabrication, the 625 voxels were fabricated at the 10 ms exposure time and 10 ms delay time, after which the piezo stage was moved according to CAD design trajectories for the next voxels fabrication. The total HTPP fabrication time of the 25 × 25 periodic nanostructures was 100 ms.

D. Measurements

After HTPP fabrication, the nanostructures were characterized using scanning electron microscopy (SEM), and their optical responses were investigated using a bright-field 3D microscope (the scanning range above the glass surface was 5 μm with a 0.2-μm interval and that below the glass surface was 5 μm with 0.2-μm interval). The light distribution experimental results were compared with those of the simulation of light distribution, which involved conducting COMSOL simulation. For the light extraction experiment, white light was excited from the lamp and passed through the 325–385-nm bandpass filter. The light was then reflected using a dichroic lens, passed through a 20x objective lens, and illuminated the gold-layer nanostructures. After light extraction, the extraction light passed through a 20x objective lens, the dichroic lens, and then through a 400-nm long pass filter. The light intensity signal was obtained using an optical fiber and spectrometer after applying a long-pass filter. Fig. 3 shows this optical setup.

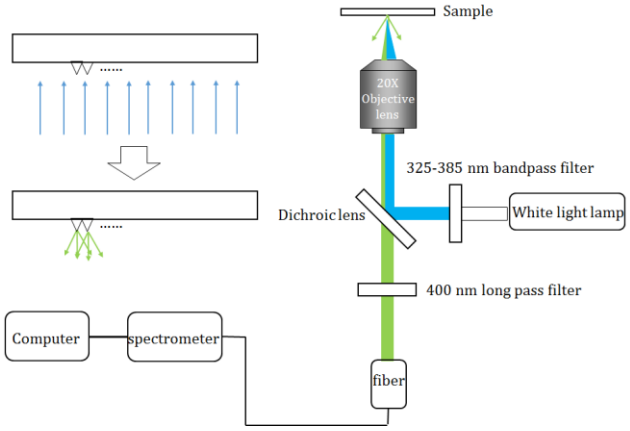

Fig. 3. Optical setup of light extraction.

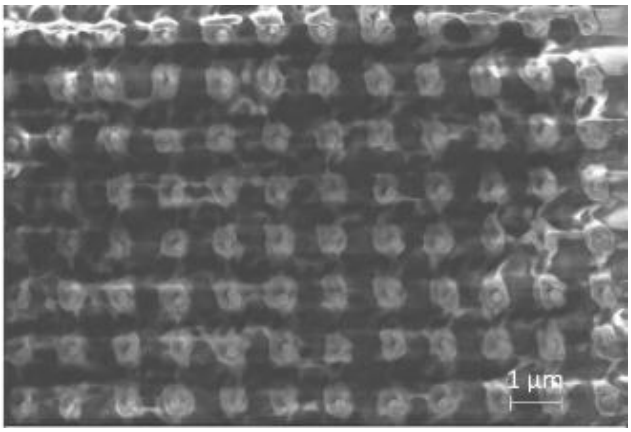

Fig. 4. SEM image of a nanostructure array.

III. Results

After HTPP fabrication, the nanostructures were investigated using SEM. In the SEM image, the 8 × 12 periodic nanostructures were a part of the 25 × 25 periodic nanostructures. Each nanostructure was integrated with five voxels, which were clearly observed in the SEM image; nanolines between nanostructures were generated in overlapping weakly polymerized regions. As shown in Fig. 4, the distance between nanostructures was 1 μm, and each nanostructure was approximately 630 ± 55 nm wide.

The light distributions shown in Fig. 5(a) and Fig. 5(b) were measured using white-light 3D microscopy, and the light distributions shown in Fig. 5(c) and (d) were simulated using COMSOL at a 545-nm wavelength. As shown in Fig. 5, the

glass surface was located at the 0-μm position, the air and structure were above the glass surface, and the glass substrate was below the glass surface. The slice images shown in Fig. 5(a) and Fig. 5(b) were taken using a CMOS camera, the range of the scanning area above the glass surface was 5 μm with a 0.2-μm interval and that below the glass surface was 5 μm with a 0.2-μm interval; the camera was attached to a moving piezo stage. For image processing, the whole slice images were reconstructed using ImageJ software to generate a 3D image. Fig. 5(a) shows a side view of the 3D image. Fig. 5(b) depicts the image in the green channel only, which is different from the color channels of the image shown in Fig. 5(a); for the image shown in the green channel, the scanning extent was restricted to 2 μm above and 2 μm below the glass surface. However, Fig. 5(c) and Fig. 5(d) were simulated using COMSOL software. The light distribution was obtained using the nanostructures that were 640 nm wide and 1000 nm high with a refractive index of 1.47. The image depicted in Fig. 5(c) was cropped from that shown in Fig. 5(d), and the extent of the cropped image was restricted to 2 μm above the glass surface and 2 μm below the glass surface. Comparing Fig. 5(b) with Fig. 5(c) indicates that the first central hot spot between nanostructures was located at approximately 910 ± 50 nm and 890 nm. In other words, the experimental central hot spot position was corresponded with the simulated position. The results of the light distribution experiment agreed with those of the simulation.

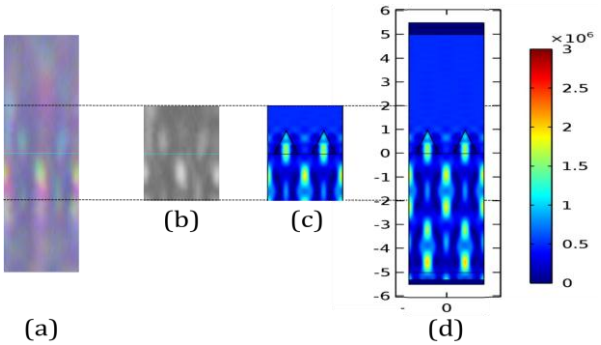

Fig. 5. 3D light distribution above (reflection) and below the nanostructure array on the glass substrate. (a) Measured using 3D microscopy, (b) image cropped from that in (a) at a extent of 2 μm above the glass surface and 2 μm below the glass surface only the green channel, (c) image cropped from that in (d) at an extent of 2 μm above and 2 μm below the glass surface, and (d) image simulated using COMSOL at a 545-nm wavelength.

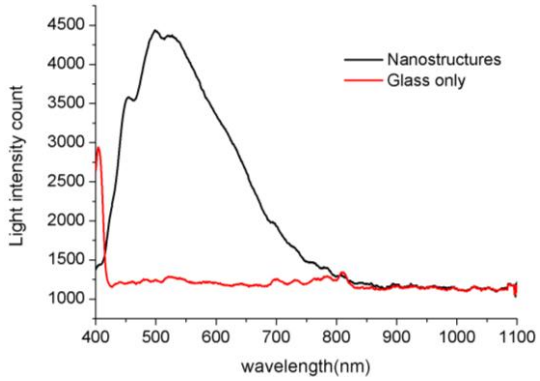

Fig. 6. Light intensity count at different wavelengths for evaluating light extraction capability of nanostructures and glass only.

After the light distribution experiment, we used electroless gold plating technology to coat the gold layer on the nanostructures only. As shown in Fig. 6, the light intensity counts for evaluating the light extraction capability were measured using the spectrometer. The highest peak of the light intensity counts was 4436.2 at a 498.54-nm wavelength. At the same wavelength, the light intensity of the glass only (without nanostructures) was 1247.1. The light extraction capability of the nanostructures was 3.6 times higher than that of the glass only.

IV. Conclusion

In this study, we demonstrated HTPP fabrication of nanostructures at a rate of mm ²per minute by using 25×25 hologram laser splitting. The results of the simulation and experimental 3D light distribution induced by the 3D nanostructures are in favorable agreement. However, the light extraction capability of the nanostructures is 3.6 times higher than that of the glass substrate only. Such high-speed fabrication of complex 3D nanostructures can be useful for applications such as light extraction or absorption in thin films or for metamaterial surfaces after electroless gold plating. Future study will entail optimizing the design of voxel arrangements for increasing light extraction efficiency in various optical surface applications.

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Chih-Lang Lin received his master's degree in power mechanical engineering from National Tsing-Hua University. He earned his Ph.D. degree in mechanical engineering from National Taiwan University. In the meanwhile, he earned another Ph.D. degree in physics of condensed material and radiation from Joseph Fourier University, France. His thesis involves two topics which are fiber Bragg grating (FBG) sensors and laser driven microsensors. In the first part, a framework for the interpretation of reflected FBG spectra under a non-uniform strain field is proposed and experimental results for a crack tip strain field are presented. In the second part, the fabrication of laser driven polymer microsensors for visconsimetry, velocimetry and micropump applications are developed. Before he created the Bio-Photonics Lab at Central Taiwan University of Science and Technology, he joined Air Liquide international group and worked in Japan to be a researcher and in Taiwan to be an operation manager. One of Dr. Lin's research interests is laser driven micromachines. He proposed a serious of elemental micromachines, such as cantilever, lever beam, spring, Archimedes screw, etc. His another interest is the fabrication of three-dimensional structured protein by using two-photon polymerization technology for detecting bio-cells such as bacteria, red blood cells, and cancer cells. More recently, he is studying the bio-mechanics of cells by using optical tweezers for the clinical diagnosis. All of the above topics are studied for contributing to Lab-on-a-chips.

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