Fabrication of two- and three-dimensional periodic submicron structures by holographic lithography with a 635 nm laser and matched photopolymer*

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2D and 3D submicron periodic structures are first fabricated by red-induced photopolymerization using a common 635 nm semiconductor laser and specially developed red-sensitive polymer material. The principle of this new photopolymer material fabrication is explained and the absorption spectra of the material are measured. This fabrication technique allows a deeper penetration into volume and larger interference irradiation area which is more than 1 cm^2. The optical design, theoretical calculations and experimental results including diffraction patterns verifying the formation of periodic structures are presented. Compared with other fabrication technologies using high-power lasers, this approach has greatly reduced the demand for laser apparatus. Therefore, it is much more accessible to most laboratories and potentially usable in holographic fabrication of photonic crystals and devices in micro electro-mechanical systems (MEMS).

Keywords: submicron periodic-structures, holographic fabrication, red sensitive polymer, red-incuced polymerization

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1. Introduction

The interest in three-dimensional (3D) micro- and nano-structures of materials is fueled by the need for photonic crystals, near-field devices for applications from electronics to photonics.[1−4] Photonic crystal (PhC) can create a photonic band gap, a region of the frequency spectra where propagating modes are forbidden in all directions, so it provides the possibility of manipulating and controlling light.[5] Naturally, the fabrication techniques for the microstructures have also been developed rapidly.[4,6−9] While system miniaturization yields enhanced integration and improved functionality, researchers have utilized photopolymerization to make the microstructures convenient, flexible, and automatic. Campbell *et al.*[2] and Kondo *et al.*[10] have fabricated three-dimensional periodic structures by using a combination of holographic lithography and ultraviolet laser-induced polymerization. Nonetheless, the commonly used ultraviolet laser, excimer laser or femtosecond laser are valuable pieces of equipment, not accessible in general laboratories, thereby limiting the development of micro-fabrication.

In this work we report for the first time on the use of a common 635 nm semiconductor laser (power < 100 mW) for making a series of submicron periodic structures by visible photoinduced photopolymerization with a new red-sensitive photopolymer recording material. Usually the red laser was considered to be unsuitable for fabrication with low intensity and power. In fact in our study a 635 nm laser can be used to achieve holographic lithography if a suitable photopolymer is synthesized. The samples fabricated verify the good formation of 2d and 3d periodic patterns by x-ray crystallography. Meanwhile, one advantage of employing a 635 nm laser over an ultraviolet laser is that the interference patterns can be visibly monitored so that optimal experimental conditions are easier to control and maintain. Besides, it can allow a deeper penetration into volume and interference in the entire irradiated area which is more than 1 cm^2. More importantly, the semiconductor laser of 635 nm may be widely used with low cost and is more accessible to most laboratories compared with the common Ti:sapphire femtosecond laser, Nd:YAG

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laser and Ar^+ laser.[11] The experiment demonstrates that this method is simple in holographic fabrication for periodic microstructures and may promote further research on photonic crystals and applications to the fabrication of micro electro-mechanical system (MEMS) devices.

In this paper the polymerization mechanism of the photopolymer material and its spectral absorption are first explained then the optical design of holographic fabrication and theoretical calculation and simulation of 2D and 3D microstructures are conducted in detail. The experimental diffraction patterns of the resulting samples are provided to verify the formation of lattices fabricated both qualitatively and quantitatively.

2. Special material of photopolymerization

The mechanism of photopolymerization is that a large number of usually identical small molecules or monomers are joined together to rapidly form a single large molecule or polymer. Red sensitive holographic polymer (RSP) material is mainly made from polymer photosensitive resin acrylamide, a kind of good monomer which keeps a double-bond structure with free radicals. To realize the holographic fabrication at red bands of light, an appropriate red-sensitive agent must be chosen and synthesized. After absorbing the optical energy, the red sensitizing agent changes into an excimer first, and then the excimer transmits energy to a photoinitiator, which would generate a free radical for polymerization. In the process of polymerization the monomers grow and combine to form macromoleculars finally.[12,13]

The detailed process of photopolymerization can be described by the following reaction formulas. Free radical chain polymerization includes three stages, i.e. photoinitiation, growth and termination. They can be written as follows: a light quantum is absorbed by red-sensitizers (S), which triggers a ground-excited state transition and changes into S^*,

$$S + h\upsilon \rightarrow S^*, \tag{1}$$

and the sensitizer of the excited state transfers the energy into the initiator (I),

$$S^* + I \rightarrow S + I^*, \tag{2}$$

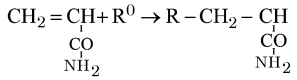
then homolytic fission of the initiator molecules of excited state (I^*) begins, cracking a molecule into two free radicals:

$$I^* \rightarrow R^{0'} + R^{0''}, \tag{3}$$

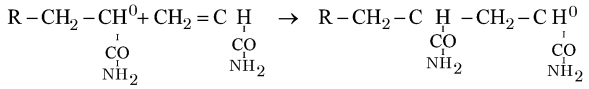
or bimolecular collision with RH reaction takes place, leading to two free radicals:

$$I^* + RH \rightarrow IH^0 + R^0. \tag{4}$$

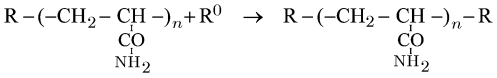
Acrylamide and free radicals will produce free radical-initiation and polymerization with the polymer chains growing simultaneously, and they will terminate when the polymer chains stop growing. Termination means the vanishing of free radical reaction activity, which is a dimolecular reaction between two free radicals. The reaction formulas are as follows:



(free radical initiation raction)



(radical polymerization)



(radical termination)

Photoinitiated polymerization turns the exposure area of RSP materials into crosslinking reticular formations, thus changing the organic molecular structures of the polymer and promoting the variations of relevant physical properties such as density. The desities in exposed and unexposed parts are different, thereby resulting in refractive index distribution of the materials and obtaining a photorefractive phase recording image which corresponds to spatial light intensity distribution. It should be particularly emphasized that this characteristic means interference patterns fabricated will be recorded in the way of refractive index profile which differs from that of the usual photoresists.

The polymer thickness coated on glass substrates is 20 μm and the photosensitivity to exposure dosage is also measured to be 1 mJ/cm^2. The absorption peaks of this photopolymer are at 610–660 nm, with absorptivity of 75%–80%. Consequently it can be used as a holographic recording material.

3. Optical design and theoretical calculation of holographic fabrication

Based on the principle of holographic fabrication, various 2D and 3D periodic structures can be constructed by varying the geometry of the interfering laser beams. As shown in Fig. 1, four beams (I, II, III and IV), which had been split from a laser, in two orthogonal planes converged to a small area of photopolymer with their corresponding incident angles and equal amplitudes, and the substrate covered with photopolymer parallel to xoy coordinate surface. The common and visible 635 nm line of the semiconductor laser (tens of mW) (from the Shanghai Institute of Optics & Fine Mechanics, China) was used in this experiment. In this way 2D lattices could be formed by an appropriate azimuthal combination of interference waves. To produce 3D interference patterns, the central beam V was added and set to be along the direction opposite to the z-axis direction while the four outer beams were placed symmetrically (90° apart) around the central beam making a common angle 30° with respect to the z-axis.

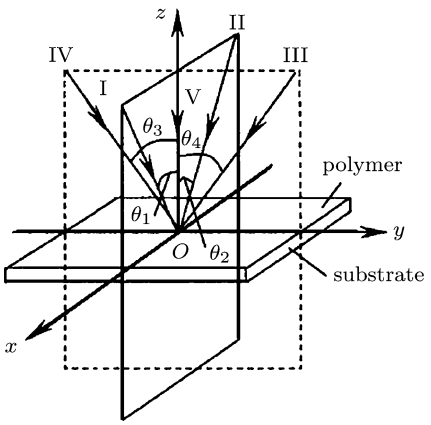


Fig. 1. Four- and five-laser-beam geometry of interference lithography.

Period and symmetry of the point lattice of the periodic interference pattern was determined by the set of selected beams and their relative phases. The set of n beams can be described as that illustrated schematically in Fig. 1. The i-th beam from the geometry was described by the azimuthal and the radial positions in the plane of the coordinates; these angles were denoted as α_i and θ_i, respectively, while the phases of the beams were denoted as ϕ_i. Thus, n recording beams can be described by using the notations of the vector form, i.e. $[\boldsymbol{\alpha}_0,\ \boldsymbol{\theta}_0,\ \boldsymbol{\phi}_0]$, $[\boldsymbol{\alpha}_1,\ \boldsymbol{\theta}_1,\ \boldsymbol{\phi}_1]$, ..., $[\boldsymbol{\alpha}_{n-1},\ \boldsymbol{\theta}_{n-1},\ \boldsymbol{\phi}_{n-1}]$. Controlling the phases of the beams allows for a fine tuning of the interference patterns.[14,15] The light intensity distribution $I(\boldsymbol{r})$ at the focus due to the interference of multiple beams can be approximated as a superposition of plane waves. For beams converging at moderate mutual angles, at which longitudinal components of the electric field parallel to the main optical axis of the system are negligible, the spatially-modulated intensity $I(\boldsymbol{r})$ is calculated from Eq. (5) to be

$$\begin{aligned} I(\boldsymbol{r}) &= \sum_{i,j} \boldsymbol{E}_i \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}_i\cdot\boldsymbol{r}+\phi_i)} \cdot \boldsymbol{E}_j^* \mathrm{e}^{\mathrm{i}(\boldsymbol{k}_j\cdot\boldsymbol{r}+\phi_j)} \\ &= \sum_{i=0}^{N-1} E_i^2 + 2\sum_{i=0}^{N-1} E_0 \times E_i \times \boldsymbol{e}_0 \cdot \boldsymbol{e}_i \\ &\quad \times \cos(\boldsymbol{K}_i \cdot \boldsymbol{r} + \phi_i) + 2\sum_{i>j=1}^{N-1} E_i \times E_j \times \boldsymbol{e}_i \cdot \boldsymbol{e}_j \\ &\quad \times \cos(\boldsymbol{K}_{ij} \cdot \boldsymbol{r} + \phi_{ij}). \end{aligned} \tag{5}$$

Since the interference pattern also depends on the beam amplitudes $\boldsymbol{E}_i$, $\boldsymbol{E}_j$, which are the complex E-field vectors, the polarizations of the four or five laser beams must be carefully adjusted. In Eq. (5), $\boldsymbol{r}$ is the coordinate vector, $\boldsymbol{k}$ is the wave-vector, and N is the number of interfering beams. The diferences in phase between the beams are denoted as ϕ_i and ϕ_j.

Obviously in holographic fabrication the shape and the size of the resulting structures were determined by the isointensity surfaces of the interference field corresponding to the exposure dosage above the photopolymerization intensity threshold. This would offer the possibility of controlling (at least to a certain extent) the size and the shape and improving the band gap property of the photonic crystals if they were made.[16]

As far as the experimental implementation was concerned, there was no principal experimental difference in fabrication between 2D and 3D samples. Figures 2 and 3 show the numerical simulation results of 2D and 3D submicron structures under 30 s exposure. The crossing square lattices in Fig. 2 and the gray volume enclosed surface in Fig. 3 represent exposure dosage above the polymerization threshold to red light. In addition, the periods of 2D and 3D lattices in (111) plane and perpendicular lattice spacings were measured to be 590 nm, 830 nm and 2.4 μm respectively.

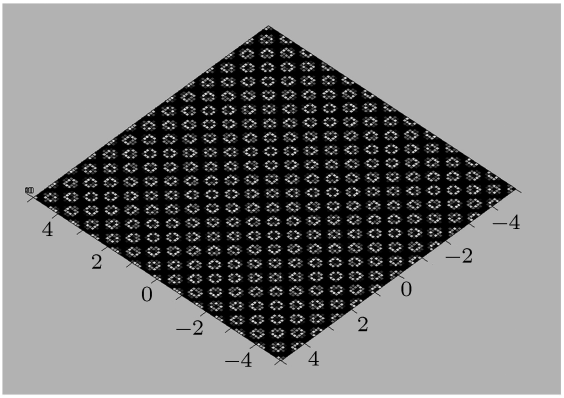


Fig. 2. Numerical distribution of light intensities for four-beam holography.

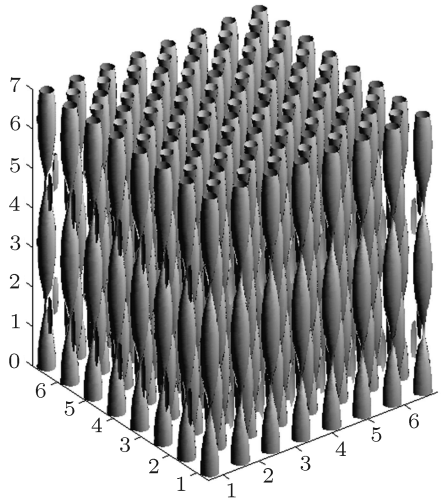


Fig. 3. Calculated 3D intensity distribution for five-beam holography.

4. Experimental verification and discussion

After exposure and polymerization, the polymer material needs post-treatment for development mechanically and chemically. The RSP-samples were rinsed in deionized (DI) water for seconds and then dehydrated in isopropanol developers of different concentrations and additives under identical experimental conditions. Finally the RSP were dried by 60°C hot blast quickly and as a result, replicas of the original interference patterns featuring a cross-connected 2D and 3D network in the sample were obtained.

As explained above, the materials resulted in refractive index distribution and a photorefractive phase recording image which corresponds to spatial light intensity distribution. Consequently the microstructures of 2D and 3D samples fabricated were recorded in the way of recording the refractive index profile. Therefore, the polymer formation and the spacings need to be measured indirectly. It is known that photonic crystals with different volume fractions and structures can display interesting optical characteristics which could conduce to accurate calculation of structures. Here the x-ray diffraction technology was employed to analyze the internal distribution of the photopolymers.[17] The 532 nm laser beam was normally incident to 2D and (111) plane of 3D samples to observe the diffraction patterns. These images are shown in Figs. 4 and 5 together with microstructure simulation graphs for further analysis, respectively.

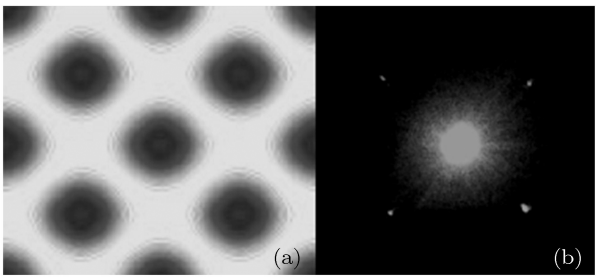


Fig. 4. Numerical simulation of 2D lattices (a) and the diffraction pattern (b).

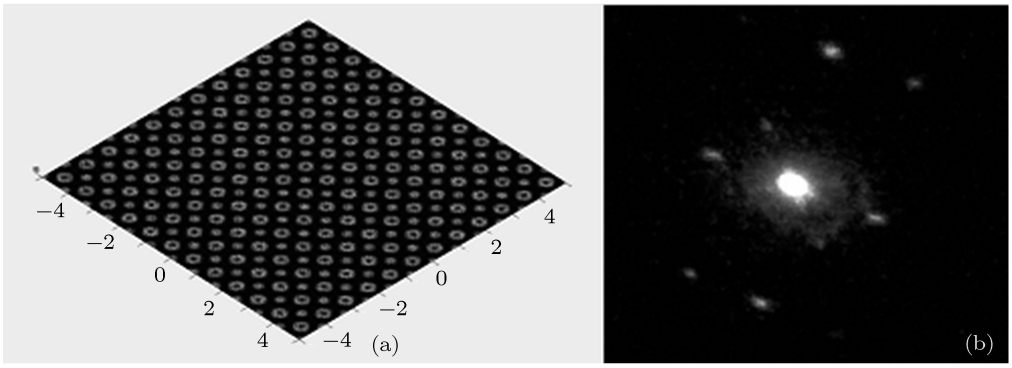


Fig. 5. 3D simulation (a) and diffraction patterns of 3d microstructure (b).

Figure 4(a) shows the plane-simulation of the micron lattices of the 2D samples fabricated. The spacing was theoretically obtained to be 590 nm from Eq. (5). With the theory of x-ray crystallography, the crossing diffraction patterns of Fig. 4(b) verify the formation of 2D square-lattice in the polymer. For a better comparision with the theoretical lattice period, we measured the 1st order diffraction angle to be 62.5°. From Eq. (6) it follows that

$$d \cdot (\sin\theta + \sin\phi) = k \cdot \lambda \quad (k = 1, 2 \ldots), \qquad (6)$$

where θ is the diffraction angle, ϕ is the incident angle, and λ is the wavelength of incident laser, the period (d) of square patterns was calculated to be 600 nm, which is in good agreement with the computer prosimulation and further confirms the formation of periodic microstructures.

The study of the 3D samples was similar to that described above, and in Fig. 5(b) the diffraction pattern corresponds to body-centered tetragonal (bct) lattice symmetry of the polymer exposed by the five-beam interference and the 1st order diffraction angle was 40°. The period of 3D lattices in (111) plane was 830 nm calculated from the diffraction equation, also confirming the simulation results of Fig. 5(a) quantitatively. Such diffraction patterns authentically assured the formation of good 3D periodic microstructures.

Exactly, photonic crystal requires a periodic structure, an appropriate tiny size and a high refractive-index contrast, which can create a photonic band gap. The samples we have fabricated satisfy most of these conditions, while we could not confirm the high contrast in the refraction index profile. If PBG of 3D photonic crystals existed, it would be located in an infrared wave band, which needs further research.

5. Conclusion

A new laser source and novel red-sensitive material are applied to holographic fabrication, which is different from what was previously reported by other researchers. We have obtained 2D and 3D nanostructure samples by using this polymer, which are in good accordance with the numerical simulations. The approach is simple in the holographic fabrication of micro-period elements and more accessible to most laboratories, providing the possibility of large-area fabrication with lower cost. These samples are sufficient for some applications such as transparent or photorefractive micro-elements in MEMS and holographic diffraction devices in integrated optical circults, no matter whether photonic band-gaps (PBG) are complete or not. Our work may also promote the development of novel 3D optical data storage materials.

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