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Fabrication of three-dimensional polymer photonic crystal structures using single diffraction element interference lithography

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This letter describes an approach for recording three-dimensional (3D) periodic structures in a photosensitive polymer using a single diffraction element mask. The mask has a central opening surrounded by three diffraction gratings oriented 120° relative to one another such that the three first order diffracted beams and the nondiffracted laser beam give a 3D spatial light intensity pattern. Structures patterned in this polymer using 1.0 and 0.56 μm grating periods have hexagonal symmetry with micron- to submicron-periodicity over large substrate area. Band structure calculations of these low index contrast materials predict photonic gaps in certain high symmetry directions. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1560860]

Three-dimensional (3D) photonic crystals (PCs) with partial or complete photonic band gaps give rise to a number of unique optical properties such as optical confinement[1] and the superprism effect,[2] which may be exploited in the future to fabricate high-density optical integrated circuits. In these synthetic crystals, the artificial periodic dielectric structure of the PC creates a photonic band gap, much as the crystal potential of a semiconductor produces an electronic band gap.[3] Complete gaps between bands correspond to forbidden wavelengths, a feature of particular utility for passive photonic devices such as filters,[4] waveguides,[5] and resonant cavities.[6] Structures with partial gaps (i.e., in restricted dimensions) may also have application in the emerging field of PC-based optical elements.[7]

Photonic band structure calculations predict partial and complete band gaps for a number of periodic dielectric lattices including 3D simple cubic, face-centered-cubic, and hexagonal-close-packed lattices.[8] Application of conventional semiconductor micromachining techniques to fabricate such PCs with near-infrared or visible band gaps is difficult and time consuming.[9] Recently, alternative approaches based on interference lithography[10] and self-assembled 3D lattices of silica spheres[11] have emerged as lower cost alternatives. Infiltration of these structures with high dielectric media allows fabrication of PCs without the constraints imposed by photolithography and dry etching.[12] Moreover, structures made by interference lithography inside polymeric liquid crystals have shown excellent optical properties despite the low index contrast difference between the polymer ($n=1.5$) and the liquid crystal ($n=1.57-1.60$).[13]

Interference lithography was first proposed and implemented by Berger *et al.* to fabricate two-dimensional (2D) hexagonal patterns in a photosensitive polymer, which subsequently served as an etch mask for transfer to a high-index silicon substrate.[14] This approach was extended by Campbell *et al.*[10] and Shoji *et al.*[15] by introducing up to two additional laser beams to create low index contrast 3D structures with face- or body-centered cubic like symmetry. This technique produced defect free, nanometer-scale structures over large substrate areas in a single step fabrication. However, fabrication strategies that rely on interference of multiple independent beams can introduce alignment complexity and inaccuracies due to differences in the optical path length and angles among the interfering beams as well as vibrational instabilities in the optical setup.

Here we describe an approach for fabricating 3D periodic structures using a single diffraction element mask to create a four-beam interference pattern recorded in a photosensitive polymer. The mask has a central opening surrounded by three diffraction gratings at 120° relative to one another. This single mask implementation can improve the alignment and stability of the optical setup, making it more robust than the multiple beam setups implemented previously.

The earlier research of Berger *et al.* showed that a single optical element consisting of three diffraction gratings oriented 120° relative to one another can produce a 2D interference pattern with hexagonal symmetry. The diameter and pitch of the high- and low-intensity regions of the interference pattern are determined by the laser wavelength and the angle of the first-order diffracted beams with respect to the incoming beam. In this letter, we introduce a fourth laser beam to provide structure in the third dimension as shown in Fig. 1. A fraction of the nondiffracted laser beam propagates through the central opening in the mask and interferes with the first order diffracted beams from the gratings.

To predict the 3D periodic structure produced by this optical element, we modeled the spatial intensity distribution I of the interference pattern from four coherent beams with arbitrary intensity, polarization, and angle:

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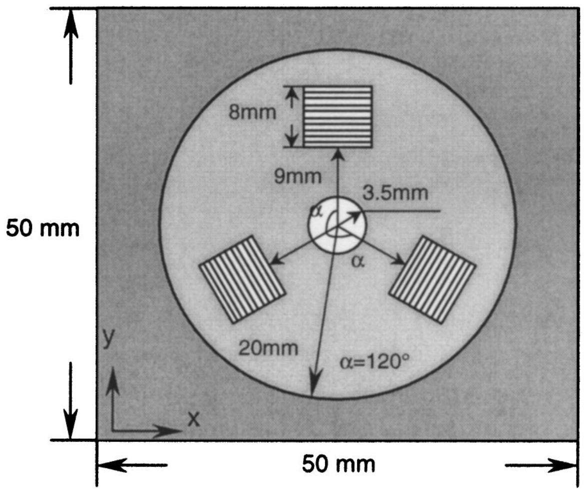

FIG. 1. Schematic representation of the diffraction element used to produce the 3D periodic structure in a photosensitive polymer.

$$I=\frac{1}{2}E_0^2+\frac{1}{2}E_1^2+\frac{1}{2}E_2^2+\frac{1}{2}E_3^2+[E_0\cdot E_1\cos(k_0r-k_1r)$$
$$+E_0\cdot E_2\cos(k_0r-k_2r)+E_0\cdot E_3\cos(k_0r-k_3r)$$
$$+E_1\cdot E_2\cos(k_1r-k_2r)+E_1\cdot E_3\cos(k_1r-k_3r)$$
$$+E_2\cdot E_3\cos(k_2r-k_3r)].$$

E_i is the maximum E-field amplitude and k_i is the wave vector of ith wave.

The 3D structures predicted for interference of four 355 nm laser beams with polarization parallel to the y axis at angles corresponding to those produced by diffraction elements with grating periods of 1.0 and 0.56 μm are shown in Figs. 2(a)–2(b). We accounted for the change in laser wavelength and interference angle within the polymer film relative to that of air assuming a polymer index of refraction $n=1.6$. The shaded areas correspond to regions where the intensity exceeded 45% of its maximum value, which is near the sensitivity threshold of the photosensitive polymer used in our experiment. Experimentally, regions of low intensity correspond to air voids, while regions of high intensity produce the interconnected 3D polymer structure.

The structure has a hexagonal lattice with an in plane lattice spacing of 1.15 (or 0.65) μm and a perpendicular lattice spacing of 8.9 (or 2.7) μm for diffraction masks with grating periods of 1.0 (or 0.56) μm, respectively. The polarization of the incident light defines a preferred axis in space, which then produces a basis that reduces the point group symmetry of the dielectric structure to orthorhombic, but the effect is very small and is irrelevant for the threshold intensities considered here. The underlying Bravais lattice remains hexagonal. The features are slightly elongated with an approximate aspect ratio (i.e., feature diameter-to-length) of 6.5 and 4.0, respectively. The aspect ratio is a function of the angle between the nondiffracted beam and the three diffracted beams, which is modified by changing the grating period. This approach can be readily extended to smaller grating pitch to achieve 3D PC structures with sub-0.5 μm pitch, which is of interest for fabricating PCs at visible and near infrared wavelengths.[16]

The optical setup used to fabricate the 3D PC polymer structure is similar to that reported in Ref. 17, with laser source, beam expander, and single diffraction element. The third harmonic of a Nd:yttritium–aluminum–garnet laser (Spectra-Physics Pro-Series 250) that generates 355 nm, 10 ns pulses at repetition rate of 10 Hz was used as the laser source. The diffraction element consisted of a mask with a 7 mm diameter central opening surrounded by three 8×8 mm^2 diffraction gratings with periods of 1.0 or 0.56 μm oriented 120° relative to one another. These phase gratings were fabricated in a thin polymer film on optically flat glass plates using a conventional holographic technique.[18] The energy diffracted in the first order beams is approximately 25%–30% of the total incoming energy, which is four to five times higher than for amplitude gratings. This lowers the exposure time of the photopolymer and makes the recorded structure less vulnerable to vibrational distortions.

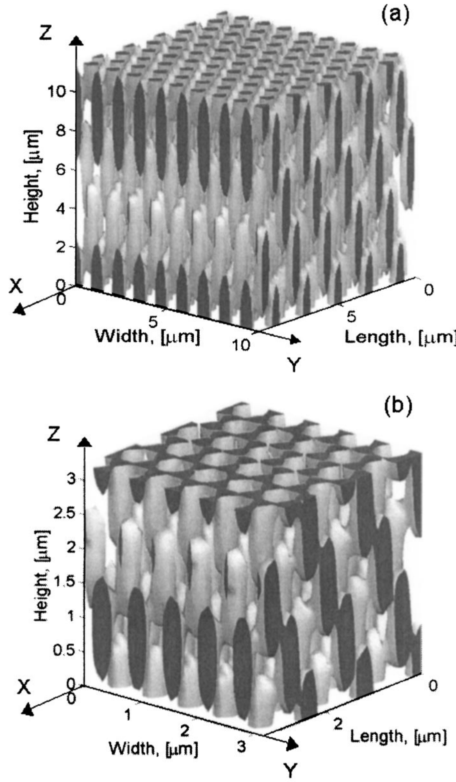

FIG. 2. Calculated light intensity distribution created by interference of four beams using the single diffraction element mask with (a) 1.0 μm period, and (b) 0.56 μm period gratings. The shaded regions correspond to all points where the intensity exceeded 45% of its maximum value.

The samples used to record the 3D structure were 1-mm-thick glass substrates coated with SU8 photoresist (MicroChem Corp.), which is a negative tone polymer sensitive at 355 nm. The photoresist was spun onto the glass substrates at 1200 rpm for 20 s, and soft baked on a hot plate for 3 min at 65 °C and 7 min at 95 °C to achieve a film thickness of 30 μm. During exposure, the samples were placed 37 mm behind the mask, at the focal plane of the interference pattern. The photoresist was exposed for 2 s, followed by a post exposure bake for 1 min at 50 °C and for 5 min at 95 °C. Developing the photoresist in PGMEA developer (MicroChem Corp.) for 10 min and rinsing with isopropyl alcohol removed regions illuminated with low intensity light.

Scanning electron microscope (SEM) images of the re-

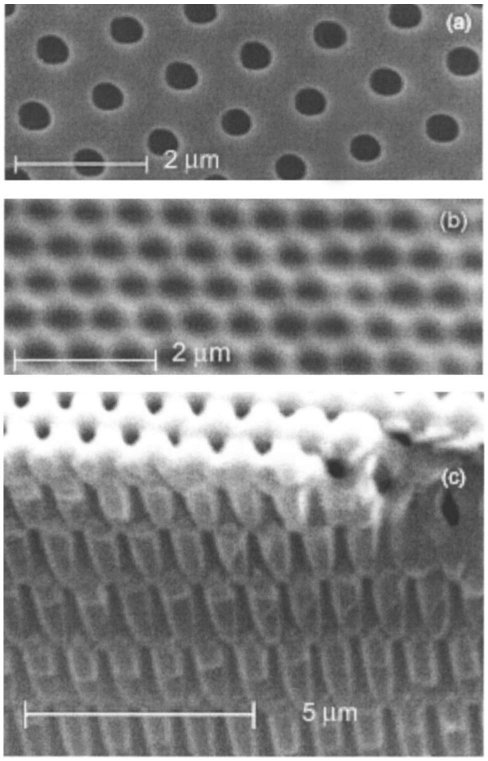

FIG. 3. SEM images of the 3D periodic structures fabricated using the diffraction mask (a) top view with 1.0 μm period, (b) top view with 0.56 μm period, and (c) cross-sectional view with 1.0 μm period. This image has large sample tilt and was not used to measure the perpendicular lattice constant.

sulting 3D polymer structure fabricated using the mask with 1.0 and 0.56 μm grating periods are shown in Figs. 3(a)–3(c). These results confirm that the single diffraction element setup can be used to create uniform 3D structures in the $x-y$ plane over large substrate area (e.g., $>1.0\ \mathrm{cm}^2$) with well defined features throughout the depth of the polymer. For the structure fabricated using the mask with 1.0 (or 0.56) μm period gratings, the in-plane lattice spacing as determined by SEM was approximately 1.2 (or 0.65) μm, which correspond well to the theoretical values. The perpendicular lattice spacing measured by cross-sectional SEM for the sample fabricated using the 1.0 μm mask was approximately 8.5 μm. This small discrepancy between the measured and calculated value could be due in part to residual tilt that remained during SEM measurement as well as a difference between the actual and theoretical index of refraction of the SU8 polymer.

To predict the photonic properties of this structure, fully vectorial eigenmodes of Maxwell's equations with periodic boundary conditions were computed by preconditioned conjugate-gradient minimization of the block Rayleigh quotient in a planewave basis.[19] The dielectric function was constructed by setting the shaded areas in Fig. 2 to $n=1.6$, and all other points to $n=1.0$. Figure 4 shows photon dispersion curves for the structure fabricated using the 0.56 μm diffraction mask. For simplicity, an orthorhombic supercell is shown. At this low index contrast, a band gap opens in the Γ–Z direction at a frequency of 0.47, while a gap in Γ–X direction at a frequency of 0.37 is slightly overlapped by higher bands. Such polymer structures could be used directly for PC optics that do not require a complete photonic

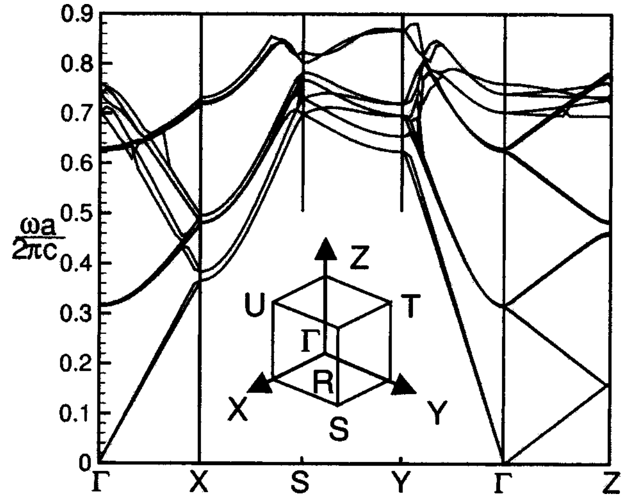

FIG. 4. Photonic band structure for the low-index contrast structure fabricated using the 0.56 μm diffraction mask. A gap opens in the Γ–Z direction at a frequency of 0.47. The gap in the Γ–X direction at a frequency of 0.37 is slightly overlapped by higher bands.

bandgap or they could be replicated by infiltration[20] or electrodeposition[17] of a high index material.

This letter describes an approach to fabricate 3D periodic structures by using a single diffraction mask to create a four-beam interference pattern patterned into a photosensitive polymer layer. Masks with a 1.0 and 0.56 μm grating period, produce micron- and submicron-scale 3D features with good definition and uniformity over large substrate areas.

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