Three-dimensional Recording by Femtosecond Pulses in Polymer Materials

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Fabrication and characteristics of two-dimensional (2D) and three-dimensional (3D) periodic structures, recorded inside the bulk of negative SU8 photoresist film by multiple-beam interference are reported. The recording was performed by ultrashort laser pulses of 150 fs duration with central wavelength of 800 nm, multiple beams were generated using a diffractive beam splitter. Intensity-dependent photomodification of the photoresist was initiated by multi-photon absorption. The development process removed the exposed regions of resist film, leaving free-standing 2D and 3D periodic dielectric structures. Detailed examination of the samples is presented, which reveals close resemblance between the features of the fabricated structures, and those of the light intensity distributions in the multiple-beam interference fields. The microfabrication method used is demonstrated to be suitable for obtaining of photonic crystal templates. Phase control of the constituent beams allowed to monitor and control the light interference pattern to be recorded. Possibility to record the diamond lattice using this method is examined and discussed.

**Keyword:** holographic recording, photonic crystals, SU8 resist, interference

1. Introduction

Development of photonics has been progressing steadily, and currently is capable of delivering sophisticated optoelectronic devices, importance of which matches that of microelectronic devices. Among the main tasks of photonics is spectral and spatial manipulation of electromagnetic radiation. Multi-dimensional diffraction gratings may be useful in realizing these tasks via dispersive and photonic band gap (PBG) effects. Various techniques for the diffraction grating fabrication exist, but two-dimensional (2D) and three-dimensional (3D) gratings can be most conveniently recorded holographically in appropriate photosensitive media, such as crystalline solid materials, liquid crystals, or photo-thermo-refractive (PTR) glasses.

Most of the earlier reports on holographic fabrication have been concentrated on 1D structures, while fabrication of 2D or 3D periodic structures has received somewhat less attention. In 1990, Burns [1] demonstrated interference technique, which allowed direct visualization of the 2D optical field intensity distribution, and a periodic arrangement of micrometer-sized polystyrene particles in the water assisted by optical forces. In this work, the periodically arranged particles were termed “optical crystals”. Berger et al. [2] have fabricated 2D hexagonal lattice in a thin layer of photoresist by interference of three beams at $\lambda =325 \text{ nm}$. The resist layer was subsequently used as the mask for reactive ion etching, and fabrication of 2D PhC in GaAs with the depth of 3 mm. The lattice period was 2.66 mm, but in principle it could be downscaled to $2\sqrt{3} = 217 \text{ nm}$. Similar techniques have been also used by others [3].

Fabrication of photonic crystal (PhC) structures by laser interference was first reported by Campbell et al. [4]. By using 355 nm nanosecond laser pulses,
they obtained 3D fcc structures with a lattice constant of 922 nm in photoresist having a thickness of several tens of micrometers. Trigonal structures were also obtained for different angles between the beams. Using the fabricated structure as a template, they fabricated an inverse periodic structure in TiO$_2$, which is known to have a higher refractive index than the photoresist. A multi-beam interference fabrication of PhCs was also performed in photopolymerizing resins, where light irradiation leads to solidification of liquid polymers [5]. 2D and 3D PhC structures recorded in SU-8 resist by the multi-beam laser interference at 380 nm wavelength using a setup based on a diffractive beam splitter (DBS) was reported earlier [6]. The initial laser beam was split by a DBS, and the selected beams were gathered by two lenses to overlap spatially in the same spot. This setup is very simple and ensures equal optical path lengths of the interfering beams, which is helpful when working with short laser pulses.

The present work focuses on the holographic recording of 2D and 3D structures in photoresist films using interference of ultrashort laser pulses, obtained from a single pulse by a DBS, and employing non-linear absorption mechanisms. Also, a principle of control of interference patterns via a phase control of the constituent beams is demonstrated.

2. Experimental details
2.1. SU-8 resist
Films of negative photoresist SU-8 (Microlithography Chemical Corp.), which is optically transparent for wavelengths $\lambda > 360$ nm (Fig. 1), were used for the recording. The photoresist was spin-coated on cover-glass plates, and had thickness of about 5-6 $\mu$m. The samples were pre-baked prior to the optical exposure. After the exposure, the samples were post-baked in order to enhance photo-initiated crosslinking reaction. The development procedure resulted in removal of the exposed regions from the sample. Typical exposure parameters used in the experiments were: average laser power before the DBS 0.21 W (Fig. 2), at the focal spot 1.67 mW (in the case of four beams). For the 150 $\mu$m diameter spot and $t_p=150$ fs, this corresponds to the 2.4 mJ/cm$^2$ pulse energy density, and $1.6\times10^{10}$ W/cm$^2$ power density. The exposure time was varied within the 5-90 s interval. The fabricated samples were inspected by a scanning electron microscopy (SEM), for which a thin layer of Au < 20 nm was coated by sputtering on the sample surfaces.

2.3. Femtosecond holographic recording
Detailed schematic picture of holographic recording setup is depicted in Fig. 2. The diffractive beam splitter (DBS) divides a single input laser beam into several beamlets, which are collected by focusing into the resist by a pair of lenses. The number of interfering pulses and their relative phases are controlled by an aperture and phase retarder plates placed between the lenses. The aperture has a number of openings, which select the required beams and block the unwanted ones. The phase retarder plates are pieces of microscope cover glass, introduced into the beams at variable orientation angles $\alpha$. A small part of the incident

![Fig. 1. Absorption spectrum of 4-$\mu$m-thick SU-8 resist film.](image1)

![Fig. 2. Optical setup for holographic recording of multidimensional periodic structures. Cover glass plates, tilted at variable angle $\alpha$ were used as phase retarders of the selected beams.](image2)
beams is split off by a larger cover glass plate, and is focused on a CCD for observation. For inspection of 3D interference patterns the CCD camera was moved along the optical axis, and different cross sectional views of the structure were examined. The lens used for focusing the beams into the sample is a dry objective lens (Olympus UApo) with 20× magnification and numerical aperture NA=0.75.

3. Results and Discussion

3.1. Phase controlled patterns

The images shown in the Fig. 3 were calculated for the phases of the two beams changed using cover glass plates as retarder element. By using setup shown in Fig 1 we have observed CCD images which were following exactly the calculated ones as depicted in Fig. 3. The patterns, which can be recorded in a photoresist or other material, have distinct periodic square structure. One may ask whether or not the images of the interference fields taken by the CCD (Fig. 2(b,c)) resemble the intensity distribution at the focus of the lens, where actual fabrication takes place. In fact, features larger than the diffraction limit can be correctly transferred into resist at the focus as we have reported recently [7]. We have corroborated that periodic intensity distributions controlled by the phases of interfering beamlets were recorded into the SU-8 with minor deviations of about 5% from the calculated ones. We have also observed that more complex periodic structures, formed by six beams can be recorded into a resist. By controlling the exposure, and recording the intensity filling ratio they can be manipulated to some extent [8, 9]. This particular feature is important for photonic crystal applications. Apart from the phase control, geometry of the recorded pattern can be controlled by selecting the distances and angles of the focused beamlets (Fig. 2). This was recently reported and used for recording by two-photon absorption recording in SU-8 resist [10].

3.2. Real 3D structures

As we have shown recently by numerical simulations [11], phase control of the interfering beamlets allows to tune the morphology of the recorded patterns. Light

Fig. 4. Hologram, recorded by five-beam interference in SU-8. The total exposure energy per pulse was 18.7 μJ, exposure time 90 s at 1 kHz repetition rate, θ = 42°, and the wavelength was 800 nm. The phase control was not implemented.
interference patterns were calculated for several geometries of DBS. Once the central beamlet is present together with at least three non-coplanar side ones, 3D patterns of light intensity distribution are obtained. However, fabrication of such 3D structures, where light intensity distribution is also modulated along its propagation direction, presents a challenge, since such structures are usually not self-supporting, and can not withstand action of the capillary forces during the development. With a proper choice of the pre-baking and post-baking procedures and by optimizing the exposure, real 3D structures, shown in Fig. 4, were finally achieved. The recording was done at 800 nm wavelength, thus multi-photon absorption was the most probable mechanism of the photomodification (see Fig. 1 for the absorption spectrum). Among the other possibilities, white light continuum (most probably via parametric four-wave mixing) and thermal radiation were also discussed as the tentative sources of exposure [9]. These topics are currently under investigation. Apart from the absorption, formation of periodic structures should be influenced by light scattering. We consider all types of refraction and reflection, which take place at the focus, and affect the passing beam, as the source of scattering. It is conceivable that photo-modified regions in SU-8 resist film act as refractive index grating, and promote formation of structures at the given periodicity. Such mechanism of self-organization is well established as the source of ripple formation during the surface ablation. To the best of our knowledge, no data concerning these circumstances has been published so far.

For best results, phases of the recording beams must be controlled depending on the recording conditions, like exposure. For example without the phase control, 3D body-centered tetragonal (bct) light interference pattern, obtained with five beams at certain higher exposure levels can record self-supporting structure, which, however, is impermeable. At lower exposures the structure becomes not self-supporting and disappears during the development [11]. This problem could be solved by the phase control. When two side beamlets out of five are phase shifted by \( \pi/2 \) using retarders, the resulting structure becomes self-supporting and permeable, and

Fig. 5. Diamond-like structure recorded by five beams hologram in SU-8 resist at 800 nm wavelength. Top (a) and slanted (b) views. Circles depict fcc structure. Energy per pulse was 18.7 \( \mu \)J, exposure time 90 s at 1 kHz repetition rate, and \( \theta = 42^\circ \).

acquires diamond lattice.

3.2. Recording of diamond-like structures by five beam interference

The phases of beamlets vary naturally within the focal spot region, which typically has 50-200 \( \mu \)m diameter. The variations mainly depend on the sample orientation and roughness of the photoresist surface. Consequently, the recorded and developed structures have different appearance at different locations after the development. In Fig. 4 surface and side cross sections were different in the neighboring regions of the focus. In the case of thin resist films with thickness smaller than 5 \( \mu \)m, and small incident angle of the side beamlets \( \theta < 60^\circ \), the period of the interference pattern along the propagation direction became larger than thickness of the film. Hence, the structure could be developed after the exposure even if it had bct morphology. Figure 5 shows such structures, which have unintentionally (because phases of the beams were not controlled) acquired diamond-like morphology. In this particular location of the developed film, phases of the interfering beamlets had phase differences required for a diamond-like pattern to occur.
Fig. 6. Recording of diamond-like structure by five-beam interference at the wavelength of 400 nm, where single-photon absorption is significant. Cross-sectional views of the structure taken by optical confocal microscopy. The top image depicts cross-section along the z-axis direction (along propagation of the recording beams), and the bottom images show xy-plane cross-sectional images taken at z coordinates which correspond to different atomic planes.

Here, the term “diamond-like” is used, because for the given recording geometry tetragonal (with axial lattice period larger than lateral period) rather than cubic 3D lattices were obtained, whereas real diamond structure must have face-centered cubic (fcc) cell symmetry.

The expected locations of “photonic atoms” for a fcc (or fct) structures are emphasized by the circles in Fig. 5. As one can see, the actual structure was more feature-rich than expected. In a slanted view (b) we can recognize twinning of the structure along the direction of light propagation. Similar “inter-weaving” should take place in diamond (and diamond-like) structures. Our focusing conditions corresponded to the axial period of the structure being 5.7 μm, larger than the thickness of the SU-8 resist film. Thus, we could assume that the phases of five beamlets at this particular film location were close to those required for a diamond-like pattern to be formed. In experiments described below, similar diamond-like patterns will be obtained by the one-photon absorption-induced photo-modification without the phase control of the interfering beams.

3.3. Diamond-like structure recorded via single-photon absorption

Because phases of the recording beams are not constant over the entire lateral cross section of the irradiated area, practical demonstration of recording via single-photon absorption is difficult. Despite these difficulties we have succeeded in recording diamond-like structures. This is shown in the images in Fig. 6, which were taken using optical confocal microscopy. The recording was done with femtosecond pulses having 400 nm central wavelength. Since the spectral width of the pulses is approximately 10 nm (FWHM), single-photon absorption is already significant, and it is difficult to develop the exposed structures evenly. The wavelength of 400 nm was chosen in order to ensure better cross-linking of the structure. The experiments have proven, however, that the fundamental absorption resulted in too extensive cross-linking. Either single or two-photon exposures were used, and light irradiation as well as photoresist spin-coating conditions were carefully adjusted. For further progress in the fabrication, pre-baking, post-baking, and development conditions should be optimized further in the future experiments.

XY plane cross-sections shown in Fig. 6 demonstrate explicitly the diamond-like character of the obtained cross-linked structure. Circles in Fig. 6 mark the locations of “photonic atoms” in the neighboring planes and, it is easy to recognize, their diamond-like ordering.

4. Conclusion

We have demonstrated two novel features, which can be implemented to control the morphology of structures recorded in photoresist by multi-beam interference. First, phase control of the interfering beams allowed to smoothly transform the interference patterns under constant monitoring, and to record the required patterns in photoresist or other media. Second, we have achieved recording of real 3D structures by five beam interference (four side
beamlets plus the central one).

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References