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# Patterned polymer photonic crystals using soft lithography and holographic lithography

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### Abstract

We fabricated patterned polymer photonic crystals by holographic lithography in conjunction with soft lithography. A patterned SU-8 photoresist film was created by preformed pattern of a hard-baked SU-8 photoresist, transferred by a PDMS mold. Then, four-beam holographic exposure carved 3D photonic crystal structures onto the patterned photoresist. Because of refractive index matching of the photoresist and the hard-baked photoresist, scattering, which might have caused a distortion of interference pattern, did not occur. Eventually, an f.c.c. polymer structure with a line pattern was successfully created after development.

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#### 1. Introduction

Photonic crystals (PCs) are optical materials whose refractive index is modulated with a period comparable to the wavelength of light. The fabrication of PCs has attracted a great attention because of their unique optical properties, especially photonic bandgaps (PBGs). Generally, a polymeric substrate such as a photoresist is carved into periodic microstructures, which are used as templates for novel materials. Periodic structures in two-dimensions (2D) and three-dimensions (3D) have been made by stacking of micromachined silicon wafers [1], self-assemblies of colloids or block copolymers [2,3], and recently by holographic lithography [4]. Among these methods, holographic lithography uses standard photolithographic resists but replaces the lithographic mask with the interference pattern of multiple coherent laser beams. While this method has many advantages of photolithography such as a large areas and defect-free processing, it is possible to fabricate 3D periodic structures.

In addition to bulk photonic crystal structures, PCs containing well-defined point and line defects are attractive because they are essential to integrated photonic chips [5]. For example, PCs with line defects may be used as optical waveguides with unique properties, such as waveguiding through wavelength-scale sharp bends and large group-velocity dispersion [6]. In the case of colloidal self-assemblies, several methods have been proposed to control the growth of colloidal crystals with controllable defects using soft lithography or photolithography, i.e., self-assembly of colloidal crystals onto patterned substrates or physical confinement in microchannel arrays [7,8]. Soft lithography applies an elastomeric stamp to generate or transfer the pattern and offers a simple and cost-effective technique [9]. Here, we combined

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holographic lithography and soft lithography for patterned 3D polymer PCs. We made tailored defects with soft lithography and then, created 3D periodic structures with holographic lithography.

#### 2. Experimental

The basic material in our experiments is SU-8 photoresist, which contained epoxy-based resin (SU-8, glycidyl-ether-bisphenol-A novolac polymer), photoinitiator (octoxyphenylphenyliodonium hexafluoro antimonate) and photosensitizer (H-Nu 470, 5,7-diiodo-3-butoxy-6-fluorene, Spectra Group Ltd.), all dissolved in r-butyrolactone. To optimize the contrast of the photoresist, we controlled the weight percent of the photosensitizer, which donates electrons when excited by visible light and consequently extracts proton ions from the monomer [10]. Previously, pattern contrast has been optimized with an aliphatic amine such as triethylamine by termination of cationic polymerization due to its high basicity [4,11]. However, in our experiments we found that excessive use of aliphatic amine had a detrimental effect on the photosensitizer (causing red-shifting of the photosensitizer's absorption spectrum, although the mechanism is not yet clear) and made the photoresist unusable within a few hours. Fig. 1 shows the sensitivity curve of the SU-8 photoresist as a function of the exposure dose for grating patterns constructed by two-beam interference and subsequent lithographic process [12]. Here, the sensitivity represents the normalized pattern contrast defined as the feature size (d) scaled by the feature distance (p). The contrast of a negative-photoresist pattern is related to the rates of both polymerization and dissolution by a developer solution. A steeper change of polymerization with the dose energy will create a higher contrast of the pattern. Therefore, the slopes of the sensitivity curves in Fig. 1 indicate that the photoresist with 0.5 wt.% photosensitizer creates a high contrast pattern.



Fig. 1. Sensitivity curve of prepared SU-8 photoresist with three different weight percents of photosensitizer and 2.5 wt.% photoinitiator.

#### 3. Results and discussion

Fig. 2 shows our experimental procedure. The PDMS mold was placed on the surface of a pretreated glass substrate to form a network of empty channels between the mold and glass [13,14]. A few drops of the SU-8 photoresist were then placed at the open ends of the channels, and this liquid spontaneously filled the channels by capillary action (Fig. 2a). After curing the photoresist into a solid by hard baking at 200 °C after an initial baking at 65 °C, the PDMS mold was removed to reveal patterned microstructures of the polymer (Fig. 2b). A SEM image of the photoresist pattern prepared on a glass is reproduced in Fig. 3a. Then, photoresist solution was spin-coated up to cover the preformed pattern (Fig. 2c). It is noteworthy that the hard-baked photoresist did not dissolve in the photoresist solution and its refractive index (1.5929 at 633 nm, as measured from Prism Coupler Analyzer, SPA-4000) matches very closely with that of the photoresist without hard baking (1.5925 at 633 nm). Therefore, the pattern was invisible when the photoresist was coated (Fig. 3b).

The photoresist on the hard-baked photoresist channel was exposed to the laser beam through a glass substrate. The exposure was conducted with four non-coplanar Ar-ion laser beams at 514 nm (Coherent, Innova 300C) with an etalon placed inside the cavity for more stable operation. To fabricate 3D interference patterns of face-centered cubic (f.c.c.) lattice, a four-beam configuration was assembled using three beam-splitter cubes [15]. The exposure time was 0.5–1 s controlled by an electronic shutter (Oriel). After exposure, a soft bake at 65 °C for 10–15 min activated epoxide ringopening polymerization and subsequent development with 1-methoxy-2-propand acetate left behind a highly polymerized region by the holographic interference pattern (Fig. 2d). (Specifically, the transferred interference pattern is asymmetric f.c.c. with the basis elongated in the [1 1 1] direction [16].)



Fig. 2. Fabrication of line patterned PCs using soft lithography and holographic lithography. The photoresist was infiltrated into microchannel arrays of the PDMS stamp (a). Hard baking induced a fully crosslinked polymer with a replica shape of the PDMS pattern (b). Spin-casting of the photoresist solution (c), followed by the exposure to the laser beams. The 3D interference pattern was transferred onto the photoresist with the line pattern (d).

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