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.
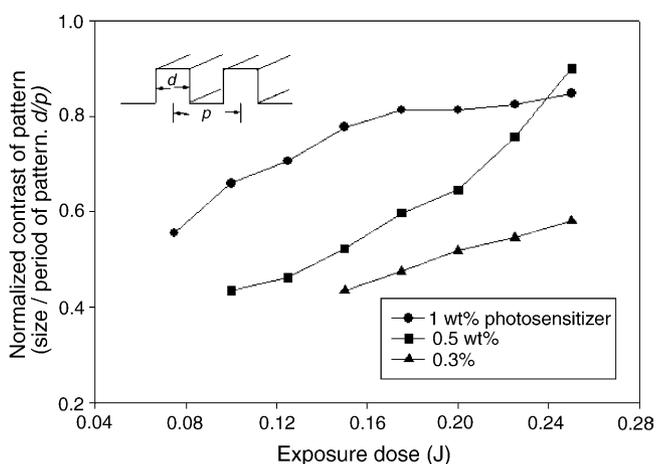

Fig. 1. Sensitivity curve of prepared SU-8 photoresist with three different weight percents of photosensitizer and 2.5 wt.% photoinitiator.

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 ring-opening 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].)
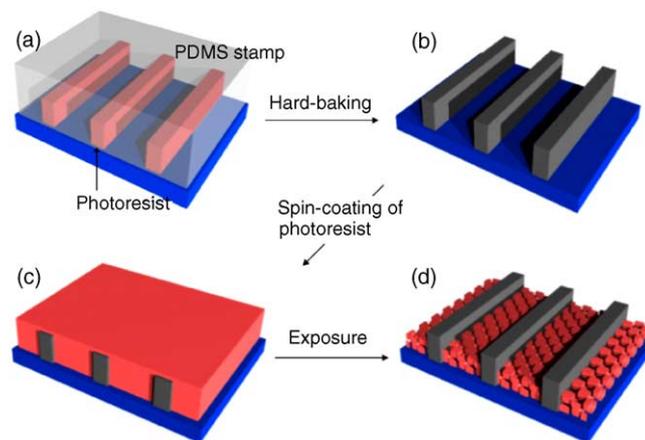

Fig. 2. Fabrication of line patterned PCs using soft lithography and holographic lithography. The photoresist was infiltrated into microchannel arrays of the PDMS stamp (a). Hard baking induced a fully crosslinked polymer with a replica shape of the PDMS pattern (b). Spin-casting of the photoresist solution (c), followed by the exposure to the laser beams. The 3D interference pattern was transferred onto the photoresist with the line pattern (d).
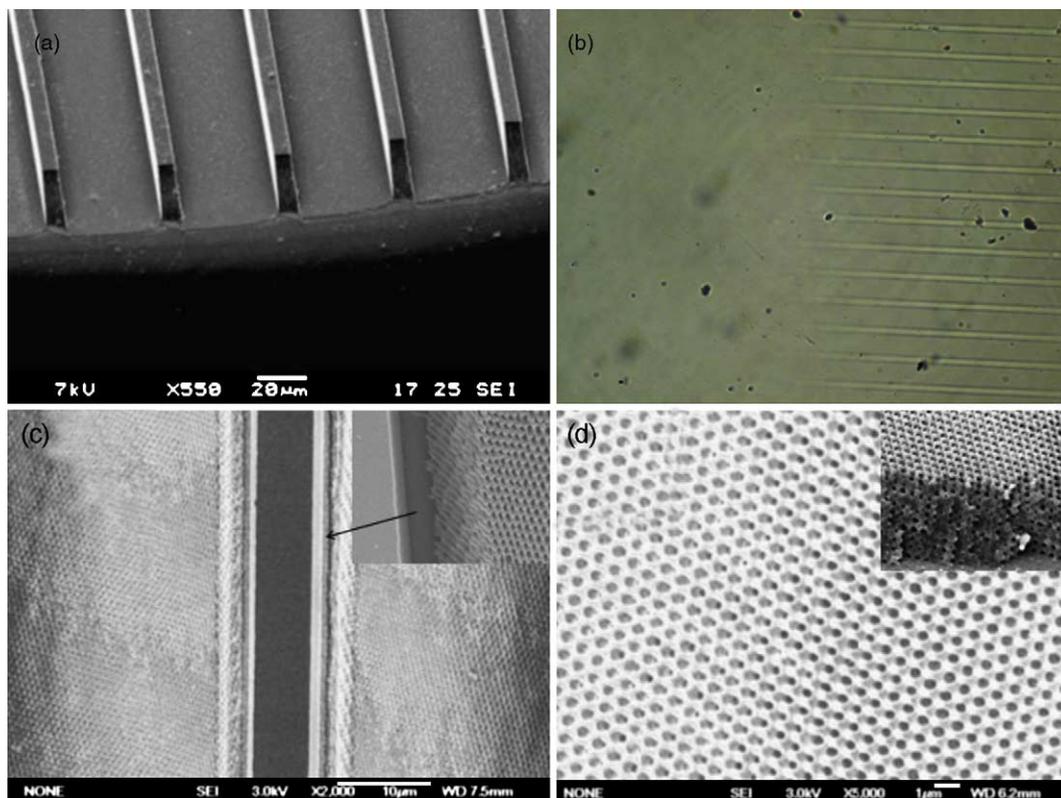
Fig. 3. (a) SEM images of hard-baked photoresist with a line pattern. (b) Photoresist spin-cast on patterned hard-baked pattern. The right half part shows the uncovered region. (c) SEM image of patterned PCs. Inset shows the boundary region. (d) SEM image of the surface and cross-section of patterned PCs of the central region.

As shown in the SEM image of Fig. 3c, patterned polymeric 3D PCs were formed by a holographic lithography. Because of refractive index matching, scattering from the patterned photoresist, which might have caused a distortion of interference pattern, did not occur significantly. Meanwhile, the cleavage between the preformed pattern and the PC structure was formed. The cleavage was caused mainly by the volume shrinkage (10–15%) of SU-8 photoresist of 3D PCs during development [17]. The surface tension of the solvent imposed a capillary force on the pore networks and created non-uniform stresses during the volume shrinkage, which eventually collapsed the porous structures. However, the cleavage can be diminished by a critical point dryer, which replaces the developer with a supercritical fluid [4b]. This is because a fluid at a supercritical state is almost inviscid with very low surface tension and vaporizes instantly passing through its critical point. Consequently, the non-uniform capillary force and viscous stresses almost vanish.

In Fig. 3d, the surface and the cross-section of the central part in the patterned PC showed f.c.c. lattices without any distortion. The top and the fractured surface correspond to a (1 1 1) and a (1 0 0) plane, respectively. Here, for the use of practical optical waveguide, the lattices of PCs should be aligned with respect to the preformed pattern for the use of optical waveguide. For the alignment, the precise translation of the pattern by a motorized stage or beam-phase shifter

can be used while the interference pattern is imaging directly [18,19].

4. Conclusions

In summary, we have demonstrated the fabrication of patterned 3D photonic crystals by holographic lithography in conjunction with soft lithography. Holographic lithography created 3D periodic structures and soft lithography made tailored defects. Because the hard-baked photoresist pattern possessed high resistance against the uncured photoresist solution and the refractive index did not change appreciably by hard baking, a crosslinked photoresist was used as a relief pattern for the holographic fabrication of patterned 3D PCs. Here, we used a line pattern as a defect. But more complicated defect geometries can be achieved straightforwardly once we have the designed PDMS stamps. Meanwhile, for practical design of the PC waveguides, the defects are necessarily enclosed by PC structures [20]. These sandwiched structures can be formed from a layer-by-layer fabrication by utilizing aforementioned property of the hard-baked photoresist. The procedure is as follows. For the bottom layer, the hard-baked PC will be prepared and then only SU-8 resin (non-crosslinkable) will be infiltrated into the PC. This layer will be used as a substrate for the subsequent fabrication of

the designed defects and a cover layer of the PC. The multilayer fabrication is currently under way in our group. In the forthcoming study, the photoresist PC structure will be inverted with a high-refractive index medium such as titania and silicon. Because the inverted structure can have full bandgaps [21,22], defects in the inverse 3D PCs can be used as the low-loss waveguide of visible and infrared light.

Acknowledgements

References

[1] E. Ozbay, E. Michel, G. Tuttle, R. Biswas, M. Sigalas, K.-M. Ho, Appl. Phys. Lett. 64 (1994) 59.

[2] Y. Yin, Y. Xia, Adv. Mater. 14 (2002) 605.

[3] A.C. Edrington, A.M. Urbas, P. DeRege, C.X. Chen, T.M. Swager, M. Hadjichristidis, L.J. Xenidou, J.D. Fetters, Y. Joannopoulos, E. Fink, L. Thomas, Adv. Mater. 13 (2001) 421.

[4] (a) M. Campbell, D.N. Sharp, M.T. Harrison, R.G. Denning, A.J. Turberfield, Nature 404 (2002) 53;
(b) S. Yang, M. Megens, J. Aizenberg, P. Wiltzius, P.M. Chaikin, W.B. Russel, Chem. Mater. 14 (2002) 2831;
(c) X. Wang, J.F. Xu, H.M. Su, Z.H. Zeng, Y.L. Chen, H.Z. Wang, Y.K. Pang, W.Y. Tam, Appl. Phys. Lett. 82 (2003) 2212.

[5] Y.A. Vlasov, X.-Z. Bo, J.C. Sturm, D.J. Norris, Nature 414 (2001) 289.

[6] M. Notomi, K. Yamada, A. Shinya, J. Takahashi, I. Yogohama, Phys. Rev. Lett. 87 (2001) 3902.

[7] Y. Yin, Y. Lu, Y. Xia, J. Mater. Chem. 11 (2001) 987.

[8] Y.-H. He, T.S. Mayer, I.-C. Khoo, I.B. Divliansky, N. Abrams, T.E. Mallouk, J. Mater. Chem. 12 (2002) 3637.

[9] Y. Xia, G.M. Whitesides, Angew. Chem. Int. Ed. 37 (1998) 551.

[10] Z. Gomurashvili, J.V. Crivello, Macromolecules 35 (2002) 2962.

[11] Y.B. Bi, D.C. Neckers, Macromolecules 27 (1994) 3683.

[12] M.J. Madou, Fundamentals of Microfabrication, CRC Press, New York, 2002.

[13] The PDMS stamp was prepared by replica molding of a polymer pattern and had arrays of $10\,\mu m \times 10\,\mu m$ micro-channels with $50\,\mu m$ width.

[14] The wettability of the SU-8 photoresist with a glass is poor, and worsens during baking. Therefore, the glass substrate was pretreated with (3-glycidoxypropyl)methyldimethoxysilane to enhance adhesion with the photoresist.

[15] The central beam was circularly polarized and incident perpendicularly to the photoresist film and the other three linearly polarized beams were oblique at $39°$ relative to the central beam and the angles between the three wave vectors of each beam were kept all at $66°$.

[16] Y.V. Miklyaev, D.C. Meisel, A. Blanco, G. von Freymann, K. Busch, W. Koch, C. ENkrich, M. Deubel, M. Wegener, Appl. Phys. Lett. 82 (2003) 1284.

[17] L. Guerin, M. Bossel, M. Demierre, S. Calmes, P. Renaud, Proc. Transducers (1997) 1419.

[18] H.M. Su, Y.C. Zhong, X. Wang, X.G. Zheng, J.F. Xu, H.Z. Wang, Phys. Rev. E 67 (2003) 056619.

[19] A. Chelnokov, S. Rowson, J.-M. Lourtioz, V. Berger, J.-Y. Courtois, J. Opt. A: Pure Appl. Opt. 1 (1999) L3.

[20] (a) Y.-H. Ye, T.S. Mayer, I.-C. Khoo, I.B. Divliansky, N. Abrams, T.E. Mallouk, J. Mater. Sci. 12 (2002) 3637;
(b) N. Tetreault, A. Mihi, H. Miguez, I. Rodriguez, G.A. Ozin, F. Meseguer, V. Kitaev, Adv. Mater. 16 (2004) 346;
(c) E. Palacios-Lidon, J.F. Galisteo-Lopez, B.H. Juarez, C. Lopez, Adv. Mater. 16 (2004) 341.

[21] G. Subramanian, V.N. Manoharan, J.D. Thorne, D.J. Pine, Adv. Mater. 11 (1999) 1261.

[22] Y.A. Vlasov, X. Bo, J.C. Sturm, D.J. Norris, Nature 414 (2001) 289.