Fabrication of Three-Dimensional Photonic Crystals Using Multibeam Interference Lithography and Electrodeposition

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Considerable research has been carried out on photonic crystals[1,2] since the concept was introduced in 1987.[3,4] However, fabrication of high-quality 3D photonic crystals still remains a challenge. Among a wide range of proposed techniques, creation of large-area, defect-free 3D polymeric templates through multibeam interference lithography,[5] direct laser writing,[6] or direct ink writing,[7] and subsequent infiltration of a high-refractive-index material into the templates[8–13] are among the most promising. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) have been used for infiltration of Si,[10–13] Ge,[14] and TiO2.[15] These conformal coating methods, however, cannot fill the 3D templates completely, reducing or eliminating the photonic bandgap in many structures including diamond,[16] gyroid,[16] and inverse woodpile photonic crystals.[14] In this communication, we demonstrate the fabrication of a high-quality 3D photonic crystal through electrodeposition into a polymer template created by multibeam interference lithography, followed by removal of the template. Complete infilling of the template is achieved through bottom-up electrodeposition.

Interference lithography is attractive because of its versatility in creating photonic crystals of many different symmetries over large areas.[5,17–22] The resulting photonic crystals are expected to exhibit excellent optical properties due to their defect-free nature. Electrodeposition is capable of growing a variety of metals and semiconductors into complex 3D geometries, as demonstrated by successful electrodeposition of inverse opal structures.[22–26] The combination of interference lithography and electrodeposition, therefore, has a great potential to produce a variety of photonic crystals with unique properties. Recently, a TiO2 replica of an interference-lithographically defined template was fabricated using electrodeposition of titania sol–gel.[27] However, as is the case in conventional sol–gel processes,[28] this technique requires calcination of infilling precursor to form TiO2, resulting in volume shrinkage and a loss of long-range order of the structure.

Here, we selected Cu2O as an infilling material because of its high volume shrinkage and a loss of long-range order of the structure.

The 3D polymer template was fabricated on a conductive, transparent indium tin oxide (ITO)-glass substrate by exposing a negative-tone photoresist, SU-8, to superimposed interference beams over a spot size of ∼3 mm. The template is required to stay in contact with the substrate for reproducible infiltration. However, swelling of SU-8 in developer solution (propylene glycol methyl ether acetate, PGMEA) often induces delamination from the substrate. In addition, the high surface tensions of the aqueous solution and electrodeposited Cu2O cause the template film to lift off during electrodeposition. To avoid these problems, the ITO substrate was treated by O2 reactive-ion etching (RIE) before coating with SU-8. Additionally, the developed template was hard-baked at 90 °C. These treatments improved the adhesion between the template and ITO, and prevented delamination during processing.

Figure 1 presents scanning electron microscopy (SEM) images of the polymer template formed via the interference lithography. The 3D polymer template created on a conductive, transparent indium tin oxide (ITO)-glass substrate by exposing a negative-tone photoresist, SU-8, to superimposed interference beams over a spot size of ∼3 mm. The template is required to stay in contact with the substrate for reproducible infiltration. However, swelling of SU-8 in developer solution (propylene glycol methyl ether acetate, PGMEA) often induces delamination from the substrate. In addition, the high surface tensions of the aqueous solution and electrodeposited Cu2O cause the template film to lift off during electrodeposition. To avoid these problems, the ITO substrate was treated by O2 reactive-ion etching (RIE) before coating with SU-8. Additionally, the developed template was hard-baked at 90 °C. These treatments improved the adhesion between the template and ITO, and prevented delamination during processing.

The cathodic electrodeposition of Cu2O[35] was potentiostatically performed at 65 °C using the ITO substrate with the polymer template as a working electrode. The electrolyte was an aqueous solution containing copper sulfate and lactic acid at pH 9. Although Cu2O could be electrodeposited over a pH range between 9 and 12, the smoothest films were deposited at pH 9. A cross-sectional SEM image of the sample after electrodeposition (Fig. 2) shows that Cu2O grew inside the template starting from

![Figure 1. SEM images of polymer template with fcc-like lattice symmetry fabricated by holographic lithography. a) Top surface and b) fractured cross-section.](image-url)
the substrate. The absences of both air voids in the Cu$_2$O layer and obvious gaps between the deposited Cu$_2$O and the template indicate that the cavity of the template was filled with Cu$_2$O completely. The thickness of the Cu$_2$O layer can be controlled by electrodeposition time. Using our deposition parameters, Cu$_2$O layers with a thickness of about 6 μm were electrodeposited in 1 h.

After electrodeposition, to maximize the contrast of refractive index in the 3D structure, the polymer template was removed by isotropic RIE using a mixture of O$_2$ and CF$_4$ for 15 min. SEM images of the resultant structure show that the template was completely removed from the 3D composite, and that a highly ordered 3D porous structure of Cu$_2$O was successfully formed (Fig. 3a and b). These SEM images also reveal that the Cu$_2$O structure has well-defined, smooth surfaces in the bulk of the structure; however, the top surface is relatively rough. The rough surface is not desirable because it causes diffuse scattering, which reduces the optical strength of the photonic crystal. We eliminated the rough surface using simple mechanical polishing. Cu$_2$O was electrodeposited all through the template. Then, the overlayer of Cu$_2$O was polished off using 50 nm alumina abrasive, exposing a flat, smooth section of Cu$_2$O/polymer composite. Finally, the polymer template was removed using RIE. The polished photonic crystal exhibited stronger iridescence than the nonpolished one, suggesting that the rough top surface that scatters light was removed and a flatter surface with a uniformly ordered structure was created. SEM images of the polished photonic crystal clearly show the formation of a smoother top surface (Fig. 3c and d).

Copper can have two oxidation states, Cu$_2$O and CuO. To confirm that the resultant photonic crystal was composed of Cu$_2$O, the sample after RIE of the template was characterized using X-ray diffraction (XRD). The XRD pattern of the photonic crystal showed only the Cu$_2$O 200 diffraction peak, except for reflections from the ITO-glass substrate (Fig. 4). It is known that Cu$_2$O bulk films electrodeposited under the same conditions without a 3D template have a (100) preferred orientation to the substrate.[31] Similar to the bulk film, the XRD of the photonic crystal indicated that crystalline Cu$_2$O with the (100) orientation was grown inside the complicated 3D structure. The XRD also suggests that there is no obvious second phase in the Cu$_2$O photonic crystal. This indicates successful electrodeposition of Cu$_2$O into the 3D template as well as successful removal of the template without conversion of Cu$_2$O to CuO.

Figure 5 presents normal-incidence reflectance spectra of the polymer template before electrodeposition and the Cu$_2$O/air photonic crystal, and compares them with calculated photonic-band structures in the $\{111\}$ direction. In the reflection spectra of the template (Fig. 5a), a peak was observed at $\sim$1.3 μm, which is in agreement with the calculated position of the (111) stop band for the template with polymer-filling fraction of 45%. This filling fraction is consistent with the estimation from the Fabry–Perot fringes, the template thickness, and the refractive index of bulk SU-8 film, 1.57.[22] The increase in the spectra background with increasing wavelength is due to the reflection off the ITO-glass substrate. The inversion of the polymer template by Cu$_2$O
increases the effective refractive index, resulting in a red-shift of the reflection peak to 2.0 μm (Fig. 5b). The peak position matches well with the band structure, assuming the exact inverse structure of the template. The peak reflectance increased from ~50\% for the template to nearly 100\% for the inverse Cu\textsubscript{2}O photonic crystal. The nearly 100\% peak reflectance, which includes a background of ~15\%, at the theoretically predicted position provides evidence for complete inversion with void-free Cu\textsubscript{2}O, and the high quality of the resultant photonic crystal. The peak reflectance is remarkably high compared with those reported for 3D photonic crystals fabricated through inversion of polymeric templates. The high reflectance is due to both the high degree of structural order within the photonic crystal and the smooth surface. We note that a similarly ordered photonic crystal with a rough surface has a much lower reflectivity. One important reason for the high quality of the structure is the low temperature of the electrodeposition-based inversion process, which enables preservation of the structure of the polymer template.

In conclusion, we have demonstrated that high-quality 3D photonic crystals can be created through electrodeposition into a polymer template fabricated by interference lithography followed by RIE of the template. The contiguous internal space of the polymer template was completely filled with crystalline Cu\textsubscript{2}O through bottom-up growth by electrodeposition, and thus, etching of the template after electrodeposition resulted in the Cu\textsubscript{2}O/air photonic crystal with the exact inverse structure of the template. The top surface of the as-electrodeposited photonic crystal was effectively smoothened by polishing. The resultant Cu\textsubscript{2}O photonic crystal showed a peak reflectance of almost 100\% at the theoretically predicted wavelength. The fabrication process established here is applicable to other polymeric templates, such as those fabricated by phase mask lithography\cite{32} and direct laser-writing.\cite{30} The complete infiltration and precise replication through our process offer further flexibility in designing photonic-crystal devices.

**Experimental**

**Fabrication of Template:** The photoresist solution was prepared by mixing 0.5 wt\% solid content of a photoinitiator, cyclopentadieny/(fluorene)iron(II) hexafluorophosphate (Aldrich), in an SU-8 solution (MicroChem, SU-8 2000 series). ITO glass with a sheet resistance of 15–30 Ω was cleaned in acetone and isopropanol, followed by RIE with O\textsubscript{2} flow (10 sccm, 10 mTorr, 1 Torr = 133.32 Pa) at 150 W for 3 min. Immediately after RIE, the SU-8 film was spin-coated (1000 rpm, 30 s) on the ITO substrate. It was exposed to four visible laser beams split from one coherent laser source (laser output of 5.4 W, frequency-doubled Nd: YVO\textsubscript{4} laser, 532 nm) and arranged in an umbrella geometry [22] for 0.5 s. The angle between the central beam and side beams was 42.5° in air, corresponding to 25° inside the unexposed photoresist. The central beam was circularly polarized, and the side beams were linearly polarized in their incident planes. After exposure, the film was post-baked at 80°C for 15 min in dry air and developed in PGMEA for 1 h, followed by rinse in isopropanol. The sample was supercritically dried with CO\textsubscript{2} from isopropanol, and then hard-baked at 90°C for 15 min.

**Electrodeposition:** Electrodeposition of Cu\textsubscript{2}O [31] was performed using a conventional three-electrode setup. A platinum plate and a Ag\textsubscript{2}AgCl in saturated potassium chloride aqueous solution (SSE) were used as counter and reference electrodes, respectively. The electrolyte was an aqueous solution containing cupric sulfate (0.2 M) and lactic acid (1.6 M). The pH of the solution was adjusted to 9 by addition of sodium hydroxide. The solution temperature was kept constant at 65°C during deposition. The Cu\textsubscript{2}O layer was grown under potentiostatic conditions at ~0.55 V versus SSE. To facilitate infilling of the hydrophobic SU-8 template with the cupric sulfate aqueous solution, the 3D template was first wetted by ethanol before electrodeposition.

**Removal of Template:** After electrodeposition, the polymer template was removed by RIE under O\textsubscript{2} and CF\textsubscript{4} flows at 20 and 2 sccm, respectively, with a base pressure of 500 mTorr and a power of 200 W for 15 min. The sample was washed in ethanol briefly after RIE.

**Characterization:** XRD was performed using a Rigaku D-Max diffractometer with a Cu X-ray tube. Before measurement, Cu\textsubscript{2}O solid film deposited outside the template was shaved off from the sample so that detected signals were only from the photonic crystal and the substrate. Reflectance spectra were measured using a Bruker vertex 70 FTIR system coupled with a Hyperion 1000 microscope. A 10× objective with a numerical aperture of 0.25 was used for measurement. The collection area was limited to a 75 μm diameter spot using an aperture in the image plane of the optical path. Spectra were normalized to a silver mirror. For photonic-band-structure calculations, a model structure of the polymer template was constructed as follows [22]: the intensity distribution in the original interference pattern was calculated from the beam parameters. It was shrunk perpendicularly to the substrate to account for shrinkage during development and to match the (111) spacing, 520 nm, observed by SEM. In the modified intensity distribution, the region with higher intensity...
than a threshold was taken to be polymer and air-filled the remainder. The threshold was chosen to match the polymer filling fraction of 45%. The inverse structure of the template was taken as the model of the Cu$_2$O photonic crystal. Photonic-band structures were calculated using the MIT Photonic Bands Package\[33\], where the refractive indices of 1.57 \[22\] and 2.6 \[29–31\] were used for SU-8 and Cu$_2$O, respectively.

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