Fabrication of two-dimensional photonic crystals using interference lithography and electrodeposition of CdSe

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This letter describes a simple synthetic approach to fabricate two-dimensional midinfrared CdSe photonic crystals (PC) by electrodeposition of CdSe in a polymer template defined using interference lithography. Characterization of the transmission spectra of CdSe PCs with a hexagonal array of 1.3 \( \mu m \) diameter and 2.7 \( \mu m \) pitch air voids showed a well-defined drop in transmission at 4.23 \( \mu m \). The drop in transmission increased with incident angle, reaching a maximum of approximately 2.6 dB at 40\(^\circ\) relative to the surface normal. This two-step synthetic approach can be used to incorporate photonic crystals onto arbitrary substrates for integration into future advanced optical circuits. © 2001 American Institute of Physics. [DOI: 10.1063/1.1420584]

Recently, there has been considerable interest in investigating the unique optical properties of two- and three-dimensional (2 and 3D) photonic crystals (PCs), which consist of periodic dielectric structures with large index contrast.\(^1,2\) In these synthetic crystals, the periodic dielectric structure produces a photonic band gap, much as the crystal potential of a semiconductor produces an electronic band gap. Complete gaps between bands have been observed theoretically and experimentally for a number of periodic dielectric lattices including 2D square and hexagonal arrays,\(^3,4\) and 3D simple cubic, face-centered-cubic, and hexagonal-close-packed lattices.\(^5-7\) The unique optical properties of these PCs can be used to design a wide range of passive optical devices such as filters,\(^8\) waveguides,\(^9\) and cavity resonators.\(^10\)

A number of techniques have been used to fabricate 2D PCs, which have the greatest potential for near term application in optical integrated circuits (OICs). The most common approach involves using electron-beam lithography to define a mask with nanometer-scale periodic features on a substrate such as silicon or gallium arsenide that has a high-dielectric constant.\(^11\) The underlying substrate is removed by reactive ion etching of the unmasked regions, which results in a 2D PC with air voids in a high-dielectric background. While this method permits rapid integration of user-defined mask patterns, high-volume production on large area substrates will be limited by the throughput of electron-beam lithography. Moreover, dimensional control of the PC is constrained by the limitations of plasma etching the dielectric material. Nonlithographically defined PCs based on macroporous silicon and extruded optical fibers have also been investigated,\(^12,13\) and have the potential to alleviate some of these constraints. However, most of the alternative approaches have been used to demonstrate discrete PC devices, and may not be suitable for OIC fabrication.

In this letter, we describe a simple synthetic approach to fabricate a 2D CdSe PC by electrodeposition of CdSe in a polymer template defined using interference lithography. This two-step PC process offers many advantages over conventional PC fabrication approaches, including incorporation of materials with higher dielectric constant and integration of PCs onto arbitrary substrates. Moreover, templates fabricated using interference lithography can be extended to integrate defect structures in 2D and can also be used to fabricate interconnected 3D PCs.\(^14\)

The first step of our PC synthesis involves forming the polymer template by exposing photoresist to the first-order diffraction pattern created by three-beam laser interference. The technique used to produce the periodically modulated light intensity pattern is similar to that first proposed and implemented by Berger et al. to define thin photoresist etch masks for the transfer of 2D PCs patterns into a silicon substrate.\(^15\) In our research, the diffraction pattern is produced with the optical arrangement in Fig. 1, which is comprised of a collimated Nd:YAG laser beam impinging on a mask that has three gratings oriented 120\(^\circ\) relative to one another. Each grating has 2 \( \mu m \) wide, 4 mm long features separated by 2 \( \mu m \). The sample is exposed by placing it at the focal point of the diffraction pattern, yielding a hexagonal array of photoresist columns with a diameter and pitch of 1.3 and 2.7 \( \mu m \) in negative-tone photoresist. The inverse pattern containing a hexagonal array of air voids can be fabricated with the same mask by using a positive-tone photoresist. This pattern creates a template that should yield a PC with a mid-infrared (IR) band gap at approximately 5 \( \mu m \).\(^16\) The band gap can be scaled towards the visible wavelength regime by reducing the dimensions of the grating and the wavelength of the laser.

In our experiments, the template was made from SU-8 negative photoresist (MicroChem Corp.) deposited on a glass substrate coated on one side with indium thin oxide (ITO). The ITO served as an optically transparent seed layer for
electrodeposition of the CdSe. The photoresist was spun on the substrate at 1500 rpm for 20 s and soft baked on a hot-plate for 1 min at 65 °C and 1 min at 95 °C to achieve a 3 μm thick film. The sample was then placed at the focal point of the diffraction pattern, which was 50 mm behind the mask plate, and was illuminated for 2 min with λ = 355 nm, 10 ns laser pulses from a Spectra Physics GCR-13 Nd:YAG laser with an intensity of 30 mWcm⁻². After exposing the sample, it was baked for 1 min at 50 °C and for 1 min at 95 °C, developed in PGMEA developer, and rinsed with isopropanol. Figures 2a and 2b show optical and scanning electron microscope (SEM) images of the resulting hexagonal array of photoresist columns, which are 1.3 μm in diameter and have a period of 2.7 μm.

The array of photoresist columns was used as a template for electrodeposition of a high-refractive index material. For that purpose, materials such as TiO₂, CdSe, PbS, and SnS₂ have refractive indices that are sufficiently high to introduce a deep or complete gap in the photonic band structure.17,18 We selected CdSe because it has suitable optical properties in the visible, near- and mid-IR regions; greater than 90% transmission at wavelengths higher than 1.00 μm, and refractive index of 2.55 at 1.00 μm. The air voids surrounding the photoresist columns were filled with CdSe by potentiostatic deposition of a CdSO₄ (0.3 M), SeO (0.7 mM), H₂SO₄ (18 M), and H₂O (18 Mohm) solution using a procedure similar to that described in Ref. 19. During the electrodeposition the potential was swept between −400 and −800 mV at a scan rate of 750 mV/s to adjust for the differences in reduction potential of the two elements. Using this method, it was possible to deposit a layer of CdSe with a nearly one-to-one stoichiometry at a rate of approximately 2 Å/scan, allowing for control of the overall thickness of the film. Following electrodeposition, the photoresist template was removed using reactive ion etching in a mixture of O₂ and CF₄. Figure 3 shows a SEM image of the resulting CdSe replica. From this image, it is evident that the CdSe deposits uniformly in the regions not protected by the photoresist.

The CdSe PC was characterized using a Bruker Equinox 55 Fourier-transform infrared spectrometer (FTIR) with a mid-IR source and DTGS detector. Spectra of the ITO substrate, the CdSe PC, and a photoresist control sample were generated by averaging 128 scans taken at a resolution of 4 cm⁻¹ and ratioing them to an air background. Figure 4 shows FTIR spectra of the CdSe PC normalized to the ITO substrate measured at 0° and 40° from normal incidence. A well-
defined drop in the transmission is observed on the CdSe PC sample for these incident angles at a wavelength of 4.23 μm. As expected, this drop increases as the angle of incidence is increased, achieving a maximum difference of approximately 2.6 dB at 40°. To verify that the drop in the transmission results from the CdSe PC, we prepared a second sample with air cylindrical voids formed in Shipley 1811 (Shipley Corporation) positive photoresist. This sample has exactly the same structure as the CdSe PC, but is made from organic material with a lower refractive index (~1.6 at 1.00 μm). The transmission spectrum of this sample is also shown in Fig. 4, and demonstrates that there is still a slight drop in the transmission at the same wavelength as measured on the CdSe sample. This suggests that the observed drop in transmission on both samples is a result of the hexagonal PC structure, with the drop becoming more pronounced as the contrast in the index of refraction is increased.

This letter describes a simple method of fabricating a 2D PC using interference lithography and CdSe electrodeposition. Characterization of CdSe 2D PCs with a hexagonal array of air voids demonstrated a well-defined drop in the transmission spectra at 4.23 μm for incident angles of 0° and 40° relative to surface normal. The drop in transmission increased with the incident angle, reaching a maximum of approximately 2.6 dB at 40°. Moreover, the transmission of polymeric PCs with an identical structure had a less pronounced drop in transmission, indicating that the drop in transmission is strongly dependent on the index contrast of the crystal. This fabrication process offers advantages over alternative approaches because it is simple and can be integrated onto arbitrary substrates. It can also be scaled to near-IR and visible wavelengths by reducing the diameter and pitch of the air voids. This can be accomplished by generating submicron interference gratings using electron-beam lithography and by using a shorter wavelength laser to create the interference pattern. Based on previous studies, the same electrodeposition process that was used in this research can be implemented to fill submicron templates.19

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FIG. 4. Transmission spectra of CdSe and polymer PCs that have been normalized relative to the ITO substrate transmission spectrum.