Multi-level diffractive optics for single laser exposure fabrication of telecom-band diamond-like 3-dimensional photonic crystals

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Abstract: We present a novel multi-level diffractive optical element for diffractive optic near-field lithography based fabrication of large-area diamond-like photonic crystal structure in a single laser exposure step. A multi-level single-surface phase element was laser fabricated on a thin polymer film by two-photon polymerization. A quarter-period phase shift was designed into the phase elements to generate a 3D periodic intensity distribution of double basis diamond-like structure. Finite difference time domain calculation of near-field diffraction patterns and associated isointensity surfaces are corroborated by definitive demonstration of a diamond-like woodpile structure formed inside thick photoresist. A large number of layers provided a strong stopband in the telecom band that matched predictions of numerical band calculation. SEM and spectral observations indicate good structural uniformity over large exposure area that promises 3D photonic crystal devices with high optical quality for a wide range of motif shapes and symmetries. Optical sensing is demonstrated by spectral shifts of the Γ-Z stopband under liquid emersion.

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References and links

1. Introduction

For practical application of three-dimensional (3D) photonic crystals in the optical domain, much simpler and lower cost fabrication techniques are desired that overcome the low throughput of semiconductor lithography [1, 2] and laser direct writing [3, 4], or the face-centered-cubic (FCC) lattice limitation of self-assembled crystals [5]. Laser holographic lithography (HL) based on interference of multiple coherent laser beams has, in part, met these criteria by providing a large variety of 3D photonic crystal templates in photo-sensitive materials.

However, the inherent vibrational instability of multiple beam splitters and mirrors over large beam paths introduce significant phase and angle errors during the exposure that distort and blur the 3D structure. A diffractive optical element (DOE) is a promising alternative approach to multi-beam HL for creating multiple interfering laser beams in various diffraction orders from a single laser beam incident on the DOE. The multiple beams are inherently phase-locked to provide stable 3D diffraction patterns in the near-field of the DOE without the instability problems of multi-beam HL [7-10]. Such near-field diffraction patterns have been captured inside photosensitive materials to provide 3D photonic crystals of low refractive index contrast which offer partial stopgaps along few preferential crystallographic directions [9]. In principle, a complete photonic bandgap could be available by inverting these templates with high refractive index materials [11, 12].

A wide range of 3D photonic crystal structures have been proposed and fabricated over the past two decades [13]. Both diamond and diamond-like structures characterized by double basis on a face-centered-cubic (FCC) or tetragonal (TTR) point Bravais lattice are very attractive for their wide complete bandgap when fabricated with high refractive index materials [14]. However, fabrication of diamond or diamond-like structures is challenging and tedious due to the double basis nature of their crystal geometry. Two dimensional phasemasks or DOEs having two phase levels (binary) inherently create 3D diffraction pattern of single basis structure arranged on body-centered-tetragonal (BCT) point Bravais lattice [7]. A diamond-like woodpile structure was first formed with diffractive optic near-field lithography by two sequential laser exposures of photoresist using orthogonally rotated 1D binary phasemasks [8, 9, 15]. To form double basis of a diamond-like structure with the two orthogonally rotated interlaced structures, a precise motion controlled stage was used along the optical axis to accurately displace one of the DOE masks between two laser exposures [9]. To overcome the inherently imprecise DOE alignment that arises between two laser exposures [8, 9], a single laser exposure fabrication of 3D photonic crystals was devised by back-to-back mounting of two linear phasemasks with crossed grating orientation. This defined a phase-tunable DOE that permitted the first single exposure near-field lithography based fabrication of the diamond-like structure [10]. The phase-tunable DOE further offered formation of a continuum of other 3D periodic structures that were tunable from the double basis diamond-like structure to a single basis structure having body-centered-tetragonal symmetry (BCT) by simply tuning the phase difference (π/2 to 0 radian) of one set of first order diffracted beams with the physical separation between the two diffractive elements as demonstrated in Ref. [10, 16]. Similar phase control mechanisms were also demonstrated in photo-polymerization of far-field multiple-beam interference pattern [17, 18]. The back-to-back connected DOE was later fabricated by two orthogonal laser exposures of two beam interference on opposite surfaces of a photoresist layer for a specific case of zero separation between two 1D gratings as shown in Fig. 3a of Ref. [19]. Although, the phase tunable near-field DOE method is versatile, it requires accurate physical separation of the two orthogonally rotated gratings in order to provide a c/4 shift between two orthogonal interference patterns required for diamond-like woodpile structure [10]. To improve fabrication reproducibility of diamond-like structure, a single-DOE device with an appropriate fixed phase-shift is therefore highly desirable. While John and co-workers proposed a phasemask design based on orthogonal placement of linear phasemasks on opposite surfaces of a single DOE substrate [20], which requires tedious etching and deposition processes on opposite surfaces of a substrate as well as precise control of separation between two 1D gratings.

In this paper, we present for the first time a single-surface multi-level DOE design with locked-in phase-shift optimized for formation of diamond-like photonic crystal structure in a single laser exposure step. Rather than rely on the precise control of substrate thickness [20], or the accurate physical separation of two DOEs for phase control [10], a phase shift was built into the single-surface DOE design which further also enables ease of etching of diffractive elements on single side of a substrate. Here, the proposed multi-level DOE was laser
fabricated on a thin polymer film to generate a woodpile near-field intensity distribution with much smaller periodicity (\(a = b = 650 \, \text{nm}\) and \(c = 2.46 \, \mu\text{m}\)) over our prior demonstrations (\(a = b = 1.06 \, \mu\text{m}\) and \(c = 6.91 \, \mu\text{m}\)) [8-10]. Diamond-like structures were fabricated in photoresist having \(\Gamma\text{-}\text{Z}\) (normal incidence) stopbands now shifted into the 1.25-1.65 \(\mu\text{m}\) telecom band from previous observations in the 3 to 5 \(\mu\text{m}\) range [9]. This new DOE design permitted a large number of layers (> 40) to form in thick photoresist, generating a record strength -30 dB stopband at 1.306 \(\mu\text{m}\). The usefulness of this stopband for refractive index sensing of liquids has been demonstrated. Finite difference time domain (FDTD) calculation of near-field diffraction patterns are corroborated by definitive demonstrations of diamond-like woodpile structure inside the photoresist. This single exposure diffractive optic lithography method facilitated high volume and reproducible fabrication of 3D photonic crystal structures for a wide range of motif shapes and symmetries. Once the master DOE was designed and fabricated, identical 3D photonic crystal templates could be reproducibly generated in large areas with only few seconds of laser exposure per sample.

2. Proposed multi-level diffractive optical element

2.1. Near-field Talbot self-imaging

The working principle of diffractive optic lithography depends on Talbot self-imaging of 2D periodic diffraction pattern that replicates the periodic DOE structure (period \(A_x\) and \(A_y\)) in the near-field or Fresnel zone. The 2D patterns repeat along the optical axis inside a medium of refractive index \(n_b\) in planes separated by the Talbot length, \(Z_T(n_b)\) [21, 22]. The DOE creates a phase distribution of the incident laser light at the interface (\(z = z_0\)) of the propagating medium that is periodic according to \(\phi(x + A_x, y + A_y, z = z_0) = \phi(x, y, z = z_0)\). This phase distribution propagates to create a 3D periodic intensity distribution satisfying \(u(x + a, y + b, z + c) = u(x, y, z)\), where \(a = A_x\) and \(b = A_y\) are lateral periodicities, and \(c = Z_T(n_b)\) is the longitudinal periodicity in medium \(n_b\). This spatial distribution of laterally and longitudinally periodic intensity distributions can be controlled by the phase profile (\(\phi(x, y, z)\)) of the diffractive structure [23, 24]. Figure 1a shows the proposed three-level DOE having a specific phase profile so that in the near-field phase-fronts of interfering diffracted beams interfere to create a diamond-like intensity distribution. The DOE is characterized by equal periodicities \(A_x = A_y = A\) and asymmetrical depths \(d_1\) and \(d_2\) of the orthogonal grooves. The DOE-patterned film has refractive index \(n_{d1}\) (blue) and \(n_{d2}\) (green) which is immersed in background refractive index \(n_b\) to define four different phase levels. For \(n_3 = n_{d1} = n_{d2}\), this reduces to three phase levels of optical thicknesses \(n_d d_2, n_d d_1 + n_b (d_2 - d_1)\), and \(n_b d_2\) in Fig. 1a.

Fig. 1. The proposed single-surface three-level DOE (a) color-coded for each phase level as defined by orthogonal grooves of periodicities \(A_x\) and \(A_y\), depths \(d_1\) and \(d_2\) and refractive indices \(n_{d1}\) and \(n_{d2}\) in a background medium of refractive index \(n_b\); and (b) laser exposure arrangement showing index matching medium \(n_i\) between DOE substrate \(n_s\) and photoresist \(n_r\) layer which is spun onto a substrate of refractive index \(n_s\).
2.2. Controlling relative shift between Talbot self-images

The groove depths, \(d_1\) and \(d_2\) of the proposed multi-level DOE are important in controlling the efficiency of various diffraction orders, which, in turn, define the motif and possibilities for linking a stable lattice together at an appropriate filling fraction. In the simple case of a binary 2D phasemask where \(d_1 = d_2\), the near-field diffraction patterns consist of two orthogonal ‘log piles’ oriented in the x and y directions that intersect in the same z plane and therefore define only a single basis structure of BCT symmetry \((c \neq a)\). Hence, different groove depths \((d_1 \neq d_2)\) are required to longitudinally offset the two orthogonal log pattern type self-images of the DOE that form in the propagating medium to form more attractive double basis diamond-like structures. As noted in [10], a offset distance of \(S = c/4 = Z_T(n_b)/4\) separates these two orthogonally rotated log-pattern type self-images axially inside the photosresist \((n_t)\) forming a double basis diamond-like structure. The respective lateral, \(a\), and axial, \(c = Z_T(n_b)\), periodicities of the resulting 3D structure in the photoresist are [9],

\[
a = \Lambda ; \quad c = Z_T(n_b) = (\lambda_d / n_b)[1 - \sqrt{1 - \lambda_d^2 / (n_b \Lambda)^2}]
\]

(1)

for normal incidence illumination by a laser beam of wavelength \(\lambda_d\). The present equation for \(c\) is exact and cannot be simplified to classical Talbot length of \(Z_T(n_b) = 2d n_b / \lambda_d\) [22], where the paraxial case of \(\lambda_d / \Lambda << 1\) is not satisfied for the large diffraction angle required here for lower \(c/a\) ratio [9]. The \(S = c/4\) offset between two orthogonally rotated logs inside photosresist \((n_t)\) can be mathematically proved to equal quarter period offset between Talbot self-images associated with two diffractive structures of groove depths \(d_1\) and \(d_2\) and given as:

\[
|d_2 - d_1| = \frac{Z_T(n_b)}{4} = \frac{\lambda_d}{4[1 - \sqrt{1 - \lambda_d^2 / (n_b \Lambda)^2}]} ; \quad \forall S = \frac{c}{4} = \frac{Z_T(n_b)}{4}
\]

(2)

where \(Z_T(n_b)\) is the Talbot length corresponding to background refractive index \((n_b)\) of the three-level DOE.

2.3. Optimized DOE design for fabrication of photonic crystal with complete bandgap

The ideal objective in the DOE design is to produce a diamond-like woodpile structure with a wide complete photonic bandgap when inverted with high refractive index materials. However, this is available only in a narrow range of axial-to-transverse periodicity ratios, \(c/a\), that further depends on the refractive index of the dielectric medium and the filling fraction [9, 14]. Diffractive optic lithography provides wide latitude for varying the \(c/a\) ratio and thereby optimizing the bandgap properties. According to Eq. (1), \(c/a\) for a specific photosresist \((n_t)\) depends primarily on the normalized wavelength, \(\lambda_d/\Lambda\). For example, a woodpile structure made with silicon \((n = 3.45)\) will provide a complete photonic bandgap only for the range 1 < \(c/a < 2.1\) for a given filling fraction of 26% [9]. The estimated maximum bandgap for this structure is \(\Delta\omega/\omega_0 = 18.5\%\) at \(c/a = 1.2\) which could be obtained by this DOE lithography method by selecting a laser wavelength to DOE period ratio of \(\lambda_d/\Lambda = 0.98 n_t\) [9]. To meet this condition for a high diffraction angle one must also avoid total internal reflection at the various interfaces by ensuring that \(n_g > 0.98 n_t\) and \(n_b > 0.98 n_t\) [9]. Clearly, high index materials are required to produce a highly symmetric \((c/a = 1.2)\) photonic crystal template. For this reason, an index matching medium \((n_i)\) is proposed between the DOE and photosresist in Fig. 1b, which allows propagation of diffracted beams with larger diffraction angles which is otherwise not possible with an air gap between the DOE and photosresist layer which also further eliminates physical contact and damage to the DOE by the photosresist. Moreover, to ensure a uniform 3D intensity distribution, DOE groove depths \((d_1, d_2)\), groove
refractive index \( (n_d) \) and background refractive index \( (n_b) \) need to be chosen in such a way that diffraction efficiencies of all 1\(^{st}\) order beams are equal [16], while also holding the groove depth difference \(|d_2 - d_1|\) to satisfy Eq. (2) for a diamond-like structure.

2.4. Practical considerations in DOE design

In targeting to meet the \( \lambda_d/\Lambda \approx 0.98n_d = 1.57 \) condition for a wide complete photonic bandgap (assumes the photoresist template is double inverted into silicon), with our present combination of \( \lambda_d = 514 \text{ nm (argon ion) laser and high resolution photoresist (MicroChem, SU-8, } n = 1.6) \) would require a small DOE period of \( \Lambda = 327 \text{ nm which is beyond our present multi-level DOE fabrication capabilities of period } \Lambda \sim 650 \text{ nm. A longer source wavelength of } \lambda_d = 1020 \text{ nm was not a desirable alternative due to the poor response of photoresist at this wavelength and lower overall expected resolutions. A compromise of a larger } c/a \text{ ratio was necessary. Commercial DOEs are now available as a binary 2D phasemask with periods typically around 1 } \mu \text{m. Multi-level masks with high resolution features on the scale of ~250 nm required here are very challenging to fabricate and must be custom fabricated. The proposed three-level DOE was directly written on thin (1 to 2 } \mu \text{m photoresist (SU-8 2002, } n_d = 1.6) \text{ by two-photon polymerization with a femtosecond laser. After testing the resolution, uniformity, and reproducibility of this method over a large writing (5 mm x 5 mm) area, a period of } \Lambda = 650 \text{ nm was selected as the minimum practical value for testing the proposed 3-level DOE design. However, according to Eq. (1), this combination predicts a large } c/a \text{ ratio of 3.78 as oppose to the } c/a = 1.2 \text{ value required for a wide complete photonic bandgap. Further effort to develop shorter period DOEs together with the use of higher refractive index media and longer wavelength laser light would lead to the more desirable } c/a = 1.2 \text{ ratio. Nevertheless, the proposed } c/a = 3.78 \text{ ratio is a significant improvement over our previous demonstration of } c/a = 6.91 \text{ which was based on a much larger grating period of } \Lambda = 1.066 \mu \text{m [8-10, 16]. The merits of multi-level DOE can thus be tested in this new high resolution regime for 3D photonic crystal fabrication. With the DOE design set to } \Lambda = 650 \text{ nm period and } \lambda_d = 514 \text{ nm laser wavelength, groove depths, } d_1 \text{ and } d_2, \text{ were optimized to balance and ideally distribute the intensities of the various DOE diffraction orders to produce uniform diamond-like 3D intensity distribution in the photoresist. Isointensity surfaces were calculated and followed with bandgap calculations as described below to optimize the bandgap properties of the expected template both in photoresist and after double inversion in silicon.}

A fixed value of \( (d_2 - d_1) = 331 \text{ nm was obtained from Eq. (2) for the } S = c/4 \text{ offset required for a diamond-like woodpile structure for this combinations of laser wavelength } (\lambda_d = 514 \text{ nm}), \text{ DOE period } (\Lambda = 650 \text{ nm}) \text{ and photoresist refractive index } (n_d = 1.6). \text{ To avoid high aspect ratio DOE grooves that might be difficult to laser-fabricate in the SU-8 photoresist } (n_d = 1.6), \text{ an air } (n_b = 1.0) \text{ background was selected for maximum index contrast. Figure 2 shows diffraction efficiencies calculated as a function of DOE groove depth } d_1 \text{ by rigorous couple wave analysis (RCWA) based commercial algorithm (GSolver Ltd.). Circularly polarized plane wave light was used to avoid the strong polarization effects [16]. The color coded unit cell of the phase profile used in the diffraction efficiency estimation is shown in the inset-(i) of Fig. 2. The area of phase element } d_2 \text{ occupies 50\% while } d_1 \text{ and background } (n_b) \text{ phase elements each occupy 25\% of the total area of the unit cell. For the present combination of laser wavelength } (\lambda_d = 514 \text{ nm}), \text{ DOE period } (\Lambda = 650 \text{ nm}) \text{ and substrate refractive index } (n_s = 1.46), \text{ there are no higher order diffracted beams } (|m|, |n| \geq 2). \text{ Due to very low diffraction efficiencies of } < 1\%, \text{ the } 1^{st} \text{ order cross beams } (|m|=|n| =1) \text{ have also been ignored. To ensure a uniform 3D intensity distribution and better local laser exposure dose control, according to Fig. 2 DOE groove depths } d_1 = 1.13 \mu \text{m, thus yielding } d_2 = d_1 + 0.331 \mu \text{m = 1.46 } \mu \text{m depth for the } c/4 \text{ offset were chosen so that diffraction efficiencies of all } 1^{st} \text{ order beams are equal for a} \)
constant \((d_2 - d_1) = 331\text{nm}\). The estimated diffraction efficiencies for this design are \(\eta_{00} = 55\%\) for the 0th order and \(\eta_{10} = \eta_{-10} = \eta_{01} = \eta_{0-1} = 10\%\) for the 1st order beams.

2.5. Finite difference time domain predictions of near-field diffraction pattern

To accurately predict the 3D periodic structures generated in the photoresist by the three-level DOE of Fig. 1, finite difference time domain (FDTD) computation was used to generate time averaged intensity distributions, \(\langle I(x, y, z) \rangle\), of the near-field diffraction pattern. Circularly polarized plane wave light of \(\lambda_d = 514\text{nm}\) was propagated through the above DOE design (\(A = 650\text{nm}\), \(d_1 =1.13\text{\mu m}\), \(d_2 =1.46\text{\mu m}\), \(n_d = 1.6\), \(n_b = 1.0\)), the glass substrate (\(n_s = 1.46\)), the index matching fluid (\(n_i = 1.604\)), the photoresist (\(n_r = 1.6\)) as arranged in Fig. 1b.

Fig. 3. Near-field intensity distribution computed by FDTD showing woodpile structure with clear offset \(S = c/4\) between two orthogonally rotated logs as expected from the three-level DOE design of \(A = 650\text{nm}\), \(d_1 = 1.13\text{\mu m}\), \(d_2 = 1.46\text{\mu m}\), \(n_d = 1.6\), \(n_b = 1.0\), \(n_s = 1.46\) and \(n_i = 1.604\). Inset (b) and (c) shows 2D intensity distribution \(\langle I(x, y) \rangle\) of two planes separated axially by \(S = c/4 = 615\text{nm}\) distance which show orthogonally rotated log-like intensity distributions as expected for a woodpile structure.
The calculated near-field intensity distribution having intensity contrast of, $C = (I_{\text{max}} - I_{\text{min}}) / (I_{\text{max}} + I_{\text{min}}) = 96\%$, was passed through a step-function threshold to closely mimic the photoresist response, yielding the 3D isointensity distribution as shown in Fig. 3. The stacking of orthogonally rotated logs in a woodpile structure is clearly evident with expected values of $a = 650 \text{ nm}$, $c = 2.46 \mu\text{m}$, and axial shift between two orthogonally rotated logs $S = c/4 = 615 \text{ nm}$ forming the double basis of a diamond-like structure. The 2D intensity distributions $<I(x, y)>$ of inset (b) and (c) clearly show the orthogonal log structure offset by the $S = c/4 = 615 \text{ nm}$ quarter period.

3. Laser fabrication

3.1. Multi-level DOE fabrication by two photon polymerization

The three-level DOE was fabricated by two photon polymerization on thin (~2 \mu m) photoresist film (MicroChem, SU-8 2002) by femtosecond laser (IMRA, \mu Jewel-D400-VR) direct writing ($\lambda = 522 \text{ nm}$, power = 100 \mu W, scan speed = 10 mm/s, pulse duration = 400 fs, repetition rate = 100 kHz and objective lens of NA = 0.9) yielding symmetric grating periods of $A_x = A_y \approx 650 \text{ nm}$ and asymmetric groove depths of $d_1 \approx 1.05 \mu\text{m}$ and $d_2 \approx 1.37 \mu\text{m}$ respectively along x and y directions. Precise depth control (~330 nm) and parallel alignment to the substrate was aided by a high precision air-bearing motion stage (Aerotech Inc., ABL1000-3D). Figure 4 shows an atomic force microscope (AFM) image of the three-level DOE fabricated by femtosecond laser direct writing after laser exposure and development. The 2D periodic structure shown in Fig. 4 was found to be uniform over most part of the actual direct laser written area of 5 mm x 5 mm. Three different phase levels of the DOE are represented by three false colors representing asymmetric groove depths of $d_1 \approx 1.05 \mu\text{m}$ and $d_2 \approx 1.37 \mu\text{m}$ respectively along x and y directions. The inset –(i) and (ii) in Fig. 4 show the $d_2$ and $d_1$ surface profiles along (a-c) and (c-d) phase segments respectively of a unit cell shown in inset-(iii). The difference in DOE groove depths $(d_2 - d_1) \approx 320 \text{ nm}$ closely satisfies Eq. (2) for shift $S \approx c/3.86$ considering the periodic relation $0 \leq S \leq c/4$.

Because of higher net laser exposure in the DOE line crossing points, an approximate ±20 nm height modulation results along the (a-b) groove direction as seen in the unit cell shown in
Fig. 4-(iii). This deviates from the uniform phase profile expected as shown in (A-B) section of the unit cell of Fig. 4-(iv), leading to an unbalance of the diffraction orders. The measured diffraction efficiencies for the 0th and 1st order beams were $\eta_{00} \approx 48\%$ and $\eta_{01} \approx 15\%$ and $\eta_{10} \approx 8\%$, respectively, for circularly polarized light which closely follows theoretical predictions of diffraction efficiencies of $\eta_{00} \approx 56.7\%$ and $\eta_{01} \approx 13.7\%$ and $\eta_{10} \approx 5.29\%$ for the inferred DOE groove depths of $d_1 \approx 1.05\,\mu m$ and $d_2 \approx 1.37\,\mu m$. This deviation from the targeted diffraction efficiencies of $\eta_{00} = 55\%$ and $\eta_{10} = \eta_{01} = \eta_{00} = 10\%$ is attributed to the (a-b) modulation noted above and differences in the fabricated groove depths $d_1 \approx 1.05\,\mu m$ and $d_2 \approx 1.37\,\mu m$ from design values of $d_1 = 1.13\,\mu m$ and $d_2 = 1.46\,\mu m$. While this imbalance in diffraction order efficiency as well as some modulation in ideal phase profile modifies the 3D near-field diffraction pattern, the strong step-function like photoresist response mitigates these differences and hence the captured near-field pattern inside the photoresist closely resembles the original predictions of the ideal DOE diffraction pattern.

3.2. Single exposure fabrication of diamond-like photonic crystal

Diamond-like woodpile three-dimensional photonic crystal were fabricated in photoresist by a single exposure of a cw argon ion (Ar+) laser at 514-nm wavelength through the three-level DOE shown in Fig. 4 and using the laser exposure arrangement of Fig. 1b. The glass substrate ($n_i = 1.46$) was first cleaned with piranha solution and baked at 200$^\circ$C for 5 min to remove moisture. To increase adhesion between the SU-8 layer and the glass substrate, a thin layer of Omnicoat (MicroChem) was spun onto the substrate following 5-sec of 500-rpm spin cycles. Since SU-8 (MicroChem, SU-8 2050) is optimized for i-line exposure (~365 nm), photo-initiator (Spectra Group, HNU470) was added to improve SU-8 absorption at 514 nm. Photo-initiator (HNU470, 0.2% wt of SU-8) and accompanied co-initiator (Spectra Group, OPPI, 2.5% wt of SU-8) were first dissolved into N,N-Dimethylacrylamide- 99% (Sigma- Aldrich Ltd.) and then SU-8 2050 was added to the solution and magnetically stirred for one day. A uniform ~30-µm thick photoresist layer was spin coated following 5-sec of 3000-rpm spin cycles. Since SU-8 (MicroChem, SU-8 2050) is optimized for i-line exposure (~365 nm), photo-initiator (Spectra Group, HNU470) was added to improve SU-8 absorption at 514 nm. Photo-initiator (HNU470, 0.2% wt of SU-8) and accompanied co-initiator (Spectra Group, OPPI, 2.5% wt of SU-8) were first dissolved into N,N-Dimethylacrylamide- 99% (Sigma- Aldrich Ltd.) and then SU-8 2050 was added to the solution and magnetically stirred for one day. A uniform ~30-µm thick photoresist layer was spin coated following 5-sec of 500-rpm which is followed by 50-sec of 3000-rpm spin cycles. This immediately followed by two steps of soft baking for 3 min at 65$^\circ$C and 10 min at 95$^\circ$C to remove volatile substances from the photoresist sample. The argon-ion (Coherent, Innova Sabre MotoFred) (514nm) laser beam was spatially filtered and collimated to provide a 6-mm diameter (Null-to-Null) beam area of 3.15 W power onto the DOE. A 7 second exposure of photoresist ($n_t = 1.6$) was made in the arrangement of Fig. 1b through the index matching fluid of refractive index $n_t = 1.604$ which was followed by two steps of post-exposure baking (3 min at 65$^\circ$C and 5 min at 95$^\circ$C) to complete the polymerization process. The baked sample was naturally cooled to the room temperature and then processed with SU-8 developer for 10 min. The developed sample was rinsed with Isopropanol (IPA) and dried with nitrogen gas. Figure 5 shows the scanning electron microscope (SEM, Hitachi S-5200) images of the top view (a) and manually cleaved cross-sectional view (b) revealing 40 layers (combining x and y oriented logs) of the photoresist structure after exposure and development. A diamond-like woodpile 3D photonic crystal structure is clearly evident with lateral periodicity of $a \approx 650$ nm and axial periodicity of $c \approx 2.32\,\mu m$ respectively, which closely match theoretical expectations of $a = 650$ nm and $c = 2.46\,\mu m$, respectively. The 6% difference in the z axis periodicity is due to shrinkage that is typical during development of SU-8, leading to a smaller observed $c/a$ value of 3.57 from theoretical $c/a$ ratio of 3.78 [9, 10, 25, 26].

In Fig. 5(b), the 3D structure is seen to form with high uniformity through the full ~25 µm thickness of the photoresist, forming 40 distinct layers. Most of the irregularities and distortions of the cross-sectional SEM image (Fig. 5(b)) of the structure came from manual cleaving of the 3D soft polymer structure using shear force. By controlling the laser exposure dose, structures with relatively wide range of filling fraction or porosity have been fabricated. The structure shown in Fig. 5 having a relatively high filling fraction of ~78% was chosen for its optical response in the telecom band as discussed in section-4. A clear vertical offset of $S = \ldots$
0.605 µm is noted between the orthogonally rotated logs in Fig. 5(b)-(iv) that closely matches the required ideal \( c/4 = 2.46/4 = 0.615 \) µm shift confirming double basis of a diamond-like structure. This corresponds well with the shift \( S \approx c/3.86 \) value inferred from Eq. (2) considering the periodic relation \( 0 \leq S \leq c/4 \) for the DOE groove depths difference of \( (d_2 - d_1) \approx 320 \) nm.

The observed structure in Fig. 5 is directly comparable with isointensity surfaces computed by the 3D FDTD method which was used to generate Fig. 3. For this calculation, the DOE unit cell was approximated with rectangular phase elements as shown by inset (iv) in Fig. 4 but using the measured AFM values of \( d_1 \approx 1.05 \) µm and \( d_2 \approx 1.37 \) µm inferred above. The resulting isointensity surfaces overlaid as inset (i) and (iii) in the respective top and cross-sectional views in Fig. 5 are seen to very closely match the SEM observations of the laser fabricated structure. Inset (iv) shows an enlarged cross-sectional view of the photoresist structure and inset (ii) shows the corresponding enlarged view of the predicted isointensity surface of inset (iii). This close FDTD prediction of isointensity-structural correspondence demonstrates the relatively high precision of femtosecond laser direct writing in creating high resolution multi-level optical surfaces with flexible tailored designs for general purpose fabrication of 3D periodic structures.

4. Optical characterization

4.1. Telecom band transmission measurement

The refractive index of the photoresist \( (n_r = 1.6) \) is too small to create a complete photonic bandgap. However, stopbands are predicted for the 3D structure shown in Fig. 5 along several crystallographic directions. The sample shown in Fig. 5 was optically probed along the \( \Gamma-Z \) direction \( (c \) axis in Fig. 5b) with a broad band source in the 1.25 µm to 1.65 µm spectral range, providing the normalized transmission spectrum shown in Fig. 6b. Transmission spectra were recorded on a fiber-to-fiber U-bench using a broadband light source (Agilent, 83437A) collimated to 500-µm diameter \( (1/e^2 \) intensity), a rotatable sample mount, and an optical spectrum analyzer (Ando, AQ6317B). All spectral recordings were normalized against a reference spectrum recorded through an identical substrate coated with an identical fully developed solid photoresist of \( \sim 30-\mu \)m thickness. At 1.306-µm wavelength, a strong -30dB attenuation stopband with narrow response of \( \sim 20 \) nm (FWHM) is observed.
The strong and narrow stopband (~20 nm) indicates that all 40 layers in Fig. 5b are collectively acting as coherent planes indicating formation of a highly uniform 3D structure throughout the thick photoresist (30 µm) and over a large area (2 mm diameter), which would otherwise be washed out by minor lattice distortions for such narrow high-order bands. This strong stopband is attributed to the large number of layers (10 unit cells along the optical axis) of the fabricated woodpile structure which strongly compensated the low refractive index contrast of the polymer-air structure. However, the long wavelength tail (1350 to 1450 nm) in the stopband is possibly related to apodization as the filling fraction decreases from the top to bottom of the photoresist layer due to gradual attenuation of the exposure laser energy.

The band dispersion relation was numerically computed using the isointensity surface of the fabricated structure shown in Fig. 5-(i)-(iii) using the plane wave expansion method [27]. This isointensity surface had been computed iteratively to match the SEM contours, the periodicity, and the ratio $c/a = 2.32/0.65 = 3.57$ observed in the fabricated structure. The computed filling fraction of $f = 76.4\%$ corresponds well with the approximate $f \approx 78\%$ value estimated from the SEM cross-sections. The calculated bands are shown in Fig. 6(a). The spectrally observed stop band at 1.306 µm closely matches the predicted stopband between the 5th and 6th bands at 1.304 µm ($a/\lambda = 0.5$) in the $\Gamma$-$Z$ direction of the energy dispersion curve. The observed ~20-nm (FWHM) bandwidth exceeds the predicted bandwidth of ~12-nm possibly due to the apodization effect described above for slightly decreasing filling fraction from top to bottom of the structure.

### 4.2. Fluid sensing with the shift in stopband

The usefulness of this strong and narrow stopband has been tested by immersing the porous crystal with ethanol while recording the transmission spectrum. An 8 µL volume of ethanol ($n = 1.34$) was uniformly sprayed on a 5 mm × 5 mm sample surface area with a micropipette. Figure 7 shows the transmission spectrum of the original stopband (t = 0-) and the stopband shifts at first immersion (t = 0+) and various times thereafter (2 to 24 min). The stopband nearly disappears on first emersion, and then recovers by shifting from ~1.26 µm wavelength back to the original location ($\lambda_0 = 1.3$ µm) after complete evaporation of ethanol.
The stopband shifting speed can be controlled with the volume of ethanol used to partially fill the open 3D crystal structure. The shift of the stopband towards lower wavelength contradicts simple Bragg prediction of shift towards higher wavelength possibly due to anomalous dispersion relation of this higher order stopband (between 5th and 6th band) in the presence of complex fluid dynamics inside dense and intricate air-pathways inside the 3D periodic structure. Nevertheless, the porous structure of the present 3D diamond-like film offer strong and narrow stopbands that are attractive as shown in Fig. 7 for optical sensing applications.

Such sensing structures can be integrated with cavities and waveguides [28, 29] for new micro-sensing applications and would thus benefit from the more reproducible and higher volume DOE fabrication method introduced in this paper.

5. Summary and discussion

This paper presents a novel single laser exposure method of fabricating diamond-like photonic crystals by multi-level diffractive optic lithography. A short-period three-level DOE (\(\lambda = 650\) nm) was laser-fabricated and applied to form 3D periodic structures in photoresist that confirm formation of thick (> 40 layers), large area diamond-like nano-structures closely matching isointensity predictions of finite difference time domain computation. Spectroscopic characterization of the polymer structure revealed a strong stopband along the \(\Gamma\)-\(Z\) direction in the telecom band that was consistent with calculated band dispersion curves for the low-index medium. Due to its porous 3D structure, such media are attractive in many sensor applications where a complete bandgap is not essential. For cases where a wide complete photonic bandgap is desirable, such structures must be inverted with a high refractive index material. However, a different DOE design is required that can further reduce the axial-to-transverse periodicity (\(c/a\), for example, to \(c/a = 1.2\) value for wide complete bandgap diamond-like woodpile structures as described in Ref. [9]. A multi-photon process based longer wavelength laser as described in [30] can be used for this purpose. Further optical engineering is therefore required to tune the present diffractive optic lithography method towards longer laser wavelength (\(\lambda_d\), shorter period diffractive structure (\(\lambda\)) and higher refractive index for the DOE grooves (\(n_d\)) and background (\(n_b\)) according to the generic design guidelines presented in the present paper. Once the master DOE was designed and fabricated, identical 3D photonic...
crystal templates could be reproducibly generated in large areas with only few seconds of laser exposure. Such multi-level DOE fabrication is easily scalable to high volume and large area manufacturing of highly uniform 3D photonic crystals.

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