DIFFRACTIVE OPTICS NEAR-FIELD LASER LITHOGRAPHY FOR FABRICATION OF 3-DIMENSIONAL PERIODIC NANOSTRUCTURES

by

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Abstract

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The main objective of the present research work is to fabricate three dimensional photonic nanostructures in photo-sensitive polymers using a novel diffractive optical element (DOE) based lithography technique. A diffractive optical element is a promising alternative device for 3D fabrication where one DOE creates multiple laser beams in various diffraction orders that are inherently phase-locked and stable for reproducible creation of 3D near-field diffraction patterns from a single laser beam. These near-field patterns are captured inside a photosensitive material like photoresist to fabricate 3D photonic crystal templates. We have demonstrated fabrication of a wide range of 3D structures having different crystal symmetries and different relative crystal axis ratios. The present work has provided 3D photonic crystal nanostructures with uniform optical and structural properties over large sample area (~3-4 mm diameter) and through large 15-50 μm thickness with large number of layers (> 40) having period 550 nm - 650 nm and feature sizes between 200 nm and 300 nm. The short exposure time and small number of process steps shows promise for scaling to very large volume fabrication, dramatically improving the throughput, quality and structural uniformity of 3D periodic nanostructures, especially over that provided by tedious and
costly semiconductor processing technology. The diffractive optics lithography is a parallel processing method that is easily scalable to generate centimeter-scale 3D nanostructures having large number of layers in several seconds. Due to low refractive index contrasts these polymer templates possess partial stopgaps along several crystallographic directions which can be practically used in several device or sensor applications where complete bandgap is not necessary. The potential usefulness of these partial stopbands for refractive index sensing of liquids has been demonstrated. These low refractive index polymer structures have been inverted with amorphous silica to convert a “soft” polymer structure to a robust “hard” structure. Further, few preliminary tests were done in fabricating 3D nanostructures into micro-fluidic channels for potential chromatography applications. The practical merits of this 3D fabrication technique will enable new practical manufacturing methods for optical and MEMS applications of 3D micro and nano structures.
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Contents

Acknowledgements iv
Published Work xxiv
List of Acronyms xxvii

1 Introduction 1

1.1 Motivation 2
1.2 New contributions 4
1.3 Overview of the dissertation 6

2 Background on three-dimensional periodic structures 9

2.1 Brief history of photonic bandgap concept 9
2.2 Bandgap theory 11
2.3 Three-dimensional periodic structures of special interest 14
  2.3.1 Diamond structure 15
  2.3.2 Diamond-like structure 16
2.4 Nano fabrication of 3D periodic structures 17
  2.4.1 Semiconductor lithography 17
  2.4.2 Self-assembly 19
  2.4.3 Direct laser writing 20
  2.4.4 Holographic lithography 22
2.5 Limitations of present 3D fabrication techniques ........................................ 23

3 Three-dimensional diffractive optics lithography .......................... 27

3.1 Introduction .................................................................................. 27

3.2 Talbot self-imaging ...................................................................... 28

3.3 Arranging Talbot self-images into a photonic crystal ................. 29

3.3.1 One-dimensional vs. two-dimensional diffractive elements ....... 30

3.3.2 Defining lattice constants .......................................................... 30

3.4 Determining depth of near-field .................................................... 33

3.5 Simulation of near-field intensity distribution ......................... 36

3.5.1 Diffraction efficiency calculation .............................................. 37

3.5.2 Isointensity calculation .............................................................. 38

3.5.2.1 Interference equation based beam re-combination method . 39

3.5.2.2 Finite difference time domain method .............................. 40

3.6 Controlling near-field intensity distribution .......................... 41

3.6.1 Effect of diffraction efficiency ................................................ 41

3.6.2 Effect of polarization ................................................................. 43

3.6.2.1 Effect on diffraction efficiency and intensity contrast ...... 43

3.6.2.2 Effect on motif shape .......................................................... 45

3.6.3 Effect of relative phase of diffracted beams ......................... 48

3.7 Photonic band calculation ............................................................. 49

3.7.1 Plane wave expansion theory .................................................. 50

3.7.2 Numerical plane wave expansion of periodic structures ...... 51
3.7.2.1 Discrete representation and classification of the 3D periodic structures ............................................. 52
3.7.2.2 Numerical representation of plane wave expansion .......... 52
3.7.3 Band calculation of 3D periodic structures ....................... 56
3.7.3.1 Dependence of band calculation on number of plane waves . 58
3.7.3.2 Dependence of band calculation on sampling frequency ..... 60
3.8 Summary ................................................................................. 61

4 Diffractive optics for fabrication of diamond-like structures 63

4.1 Introduction ............................................................................. 63
4.2 Diamond-like woodpile structure ............................................ 64
4.3 Bandgap optimization of woodpile structure .......................... 65
  4.3.1 Complete bandgap ............................................................. 65
  4.3.2 Optimized DOE parameters ............................................. 66
4.4 Diffractive optics for diamond-like structure ........................... 69
  4.4.1 One-dimensional DOE based double laser exposure method .... 70
    4.4.1.1 One-dimensional phasemask design ............................. 70
    4.4.1.2 Interlacing of two orthogonally rotated interference patterns 72
  4.4.2 Phase tunable DOE for single exposure method .................. 74
    4.4.2.1 Phase tunable DOE .................................................... 74
    4.4.2.2 Phase control principles ......................................... 75
    4.4.2.3 Finite difference time domain predictions of phase tunable
           near-field diffraction pattern ......................................... 78
  4.4.3 Multi-level 2D DOE for single exposure method ................. 79
4.4.3.1 Two-level vs. proposed three-level 2D DOE .......................... 80
4.4.3.2 Working principles of three-level DOE ................................. 81
4.4.3.3 Three-level DOE design ................................................. 82
4.4.3.4 Finite difference time domain predictions of near-field diffraction pattern ......................................................... 85

4.5 Summary .................................................................................. 88

5 Experimental ............................................................................... 89

5.1 Experimental ........................................................................... 89

5.1.1 Laser system ......................................................................... 89

5.1.1.1 Beam delivery system ...................................................... 90

5.1.1.2 Beam profile .................................................................... 91

5.1.2 Sample preparation ............................................................... 92

5.1.3 Post exposure baking and development .................................. 93

5.1.4 Characterization ................................................................... 94

5.1.4.1 Structural characterization ............................................... 94

5.1.4.2 Optical characterization .................................................. 95

6 Fabrication using one-dimensional diffractive optics .................. 97

6.1 Introduction ............................................................................... 97

6.2 One-dimensional DOE for double laser exposure method .......... 98

6.2.1 Laser exposure setup ............................................................ 98

6.2.2 Fabrication of 3D woodpile structures .................................... 99

6.3 Phase tunable DOE for single exposure method ....................... 102

6.3.1 Laser exposure setup ............................................................ 102
6.3.2 Woodpile structure with TTR symmetry ........................................... 103
6.3.3 Structure with BCT symmetry ......................................................... 104
6.3.4 Fabrication of diamond-like structure with circularly polarized light ........ 105
6.4 Optical characterization ................................................................. 107
6.4.1 Near-infrared characterization ......................................................... 107
6.4.2 Telecom-band characterization ....................................................... 109
6.5 Discussion ......................................................................................... 111

7 Fabrication using two-dimensional diffractive optics 113
7.1 Introduction ....................................................................................... 113
7.2 Fabrication of two-dimensional diffractive optics ................................. 114
  7.2.1 Two-level DOE ............................................................................. 115
  7.2.2 Three-level DOE fabrication by two photon polymerization ............. 115
7.3 Single exposure fabrication of 3D photonic crystals ............................. 117
  7.3.1 Single basis BCT symmetry structure using two level DOE ............... 118
  7.3.2 Double basis diamond-like structure using three-level DOE ............ 120
7.4 Optical characterization ....................................................................... 123
  7.4.1 Telecom band transmission measurement ....................................... 123
  7.4.2 Numerical band calculation ............................................................ 124
7.5 Comparison of proposed 3D fabrication techniques ............................ 125
7.6 Discussion ......................................................................................... 127

8 Applications of polymer 3D periodic structures 129
8.1 Introduction ....................................................................................... 129
8.2 Applications of polymer 3D photonic crystals .................................... 130
List of Tables

7.1 Comparison of the normal incident ($\Gamma$-$Z$) stopband strength ($T$) and stopband location ($\lambda_0$) of the present polymer woodpile structure with woodpile structure fabricated by other prominent groups. . . . . . . . . . . . . . 125

7.2 Comparison between four diffractive optics lithography techniques. . . . . . . 127
List of Figures

2.1 Optimized Yablonovite structure. The crystal is characterized by $\epsilon_{\text{background}} = 11.9$ and $\epsilon_{\text{pore}} = 1$. The radius of the pores is $r_{\text{pore}} = 0.332|a|_{\text{hex}}$ where $|a|_{\text{hex}}$ is the Hexagonal Bravais lattice lattice constant. The air volume fraction of the structure is $= 78\%$. Figure from [22]. 11

2.2 (a) Conventional primitive unit cell of the Hexagonal lattice together with the primitive unit vectors. (b) Brillouin zone (black) and irreducible Brillouin zone (red) of a Hexagonal lattice. Figure from [22]. 13

2.3 Band dispersion diagram of the Yablonovite photonic crystal shown in Fig. 2.1. A complete bandgap opens between bands 6 and 7, is centered at $|a|_{\text{hex}}/\lambda_{\text{vac}} = 0.39$ and has a width of 16.9 %. The location of the symmetry points used in the irreducible Brillouin zone path is shown in Fig. 2.2b. Figure from [22]. 14

2.4 (a) The diamond structure spherical atoms are placed on the lattice and nearest order neighbors are joined by cylindrical rods. Figure from [22]. (b)-(h) SEM images of diamond structure in Beetle scales. Figure from [26]. 16

2.5 (a) Tetragonal lattice with a basis formed by four identical rectangular prisms forming a woodpile structure as shown in (b). Figure from [22]. 17
2.6 Scheme (a) and SEM (b) of woodpile photonic crystals fabricated by the layer-by-layer approach. Figure from [8]. .................................................. 18

2.7 SEM of (a) silica opal and (b) Si inverted opal. Figure from [28]. .......... 20

2.8 Three-dimensional photonic crystals fabricated by direct laser writing (DLW).
(a) Woodpile structure with 40 layers and a massive wall that prevents bending and reduces distortions due to polymer shrinkage during polymerization, completely fabricated by DLW. (b) Cross and (c) top view of a different broken sample with 12 layers, illustrating the sample quality obtained with the DLW process. Figure from [9]. .................................................. 21

2.9 (a) Schematic of four beam interference setup for holographic lithography producing 3D interference pattern in the beam overlap region. Figure from [22]. SEM images from Ref. [12] of the (b) polymeric photonic crystal fabricated by exposure of photoresist to a interference pattern shown in Fig. 1A of Ref. [12] (scale bars 10 µm). Close-up view of top surface (c) and cross-section (d) of the structure shown in part (a) (scale bars 1 µm). .................. 23

2.10 Body-centred-tetragonal (BCT) symmetry structure fabricated using binary 2D DOE. Inset (a)-(c) shows top view and inset-(b)-(d) shows cross-sectional SEM views. Figure from [14]. .................................................. 25

2.11 Scanning electron microscope image woodpile-type photonic crystal recorded in the SU-8 photoresist (a) top view of the photonic structure and (b) cross-section view of the photonic structure. Figure from [15]. ............... 25

3.1 Locations of Talbot self-images behind a grating. ................................. 29
3.2 Near-field diffraction pattern of a (a) grating or 1D-DOE and a (b) 2D DOE showing a 2D log-like diffraction pattern and a 3D body-centred-tetragonal diffraction patterns respectively.

3.3 Relation between generalized Talbot length ($Z_{Tg}$) and classical Talbot length ($Z_T$) as a function of normalized wavelength inside the photoresist medium ($\lambda_m/\Lambda$).

3.4 Ray-optics picture of diffracted beam walk-off where $K_0$, $K_{\pm 1}$ represent propagation vectors of $0^{th}$ and $\pm 1^{st}$ order diffracted beams respectively.

3.5 Gradual narrowing of beam overlap region due to beam "walk-off" of a grating shown in Fig. 3.4 at arbitrary distances of (a) $L_1$ and (b) $L_2$ from grating surface as shown in Fig. 3.4.

3.6 Estimation of beam overlap region of (a) diffraction from a normally illuminated 1D-DOE and (b) normally illuminated 2D-DOE.

3.7 1D-DOE or phasemask of period $\Lambda = 650$ nm, DOE refractive index $n_d = 1.46$, background refractive index $n_b = 1$ and groove depth $d_t$ is illuminated normally with a TM polarized laser light of wavelength $\lambda_d = 514$ nm where TM polarization is defined as polarization vector parallel to the grating grooves.

3.8 Diffraction efficiency of the 1D-DOE shown in Fig. 3.7 as a function of DOE groove depth $d_t$ for DOE period $\Lambda = 650$ nm, DOE refractive index $n_d = 1.46$ and background refractive index $n_b = 1.0$. The DOE has been illuminated normally with TM polarized laser light of wavelength $\lambda_d = 514$ nm. Inset-(i) shows the unit cell used in diffraction efficiency calculation.
3.9 FDTD calculation of isointensity surface of the near-field diffraction pattern of the 1D-DOE shown in Fig. 3.7 for normal incident TM polarized plane wave light of wavelength $\lambda_d = 514$ nm.

3.10 Variation of intensity contrast ($C$) with $0^{th}$ order to $1^{st}$ order diffraction efficiency ratio ($\eta_0/\eta_1$) of the near-field intensity distribution of the 1D-DOE shown in Fig. 3.7 for same set of parameters used in the diffraction efficiency calculation in Fig. 3.8. The diffraction efficiency ratio $\eta_0/\eta_1 = 0.58 - 20$ of RCWA based diffraction efficiency prediction corresponds to DOE groove depth $d_t$ between the range $0.47 \mu m - 0.1 \mu m$.

3.11 Diffraction efficiency of the 1D-DOE shown in Fig. 3.7 as a function of DOE groove depth $d_t$ for DOE period $\Lambda = 650$ nm, DOE refractive index $n_d = 1.46$, background refractive index $n_b = 1.0$ and wavelength $\lambda_d = 514$ nm for TE, TM and circularly polarized normal incident laser light.

3.12 Variation of intensity contrast ($C$) with the diffraction efficiency ratio ($\eta_0/\eta_1$) of the near-field intensity distribution of the 1D-DOE shown in Fig. 3.7 for same set of parameters used in the diffraction efficiency calculation in Fig. 3.11 for TE, TM and circularly polarized light.

3.13 Intensity variation across a line (a) in the x and (b) in the z directions of Fig. 3.9 passing through the maximum intensity point in the respective directions calculated by FDTD.
3.14 Relative motif shape of the intensity distribution shown in Fig. 3.9 corresponding to motif shape factor $S_f = 1.63, 4.7$ and $3$ for TE, TM and circularly polarized light, respectively, for a constant diffraction efficiency ratio $\eta_0/\eta_1 = 1$ for all three polarization. ................................. 48

3.15 Change of filling fraction as a function of exposure dose of the intensity distribution shown in Fig. 3.9. .......................................................... 49

3.16 (a) Closed-packed FCC structure of air spheres ($n_f = 1$) in silicon background ($n_b = 3.45$). (b) Brillouin zone (black) and irreducible Brillouin zone (red) of a FCC lattice [22]. ........................................................... 57

3.17 (a) Analytically computed band diagram of the FCC structure shown in Fig. 3.16. (b) Band diagram of the same structure computed by the numerical PWE method where the structure has been represented by sampling frequency $F_s = 200$ samples/lattice constant. In both analytical as well as numerical PWE method 1331 plane waves have been used. ................................. 58

3.18 Variation of (a) percentage complete bandgap ($\Delta\omega/\omega_o$%) and (b) corresponding bandgap centre frequency ($a\omega_0/2\pi c$) with number of plane waves of the structure shown in Fig. 3.16a computed using both numerical PWE as well as analytical PWE method. ................................. 59

3.19 Band computation time of the FCC structure shown in Fig. 3.16a has been plotted as a function of number of plane wave and sampling frequency. ... 60

3.20 Variation of (a) percentage bandgap and (b) corresponding bandgap centre frequency with sampling frequency of the structure shown in Fig. 3.16a. ... 61
4.1 Diamond-like woodpile structure where $a$ and $c$ are lateral and axial periodicities respectively and $S$ represents centre to centre distance between two orthogonally rotated log pile structures. $R_x$ and $R_z$ represent radii of elliptical shaped logs.

4.2 Band dispersion diagram (a) for 3D woodpile structure in photoresist for values of $n = 1.6$, $c/a = 1.2$, and $f \approx 25\%$ and (b) modified dispersion diagram with the same structure after double inversion to a silicon woodpile with $n = 3.45$, $c/a = 1.2$, and $f \approx 25\%$.

4.3 Variation of the complete bandgap with $\lambda_d/\Lambda$ ratio for silicon inverted structures of silicon logs in air background ($f \approx 25\%$).

4.4 Variation of $c/a$ ratio in SU-8 photoresist ($n_r = 1.6$) with normalized wavelength $\lambda_d/\Lambda$ for different refractive index values of the incidence medium ($n_i$).

4.5 Diffraction efficiency of the phasemask as a function of groove depth $d_t$ for period $\Lambda = 1.066 \ \mu m$, DOE refractive index $n_d = 1.46$ and background refractive index $n_b = 1.0$. The phasemask has been illuminated normally with laser light of wavelength $\lambda_d = 488 \ nm$ having polarization vector parallel to the grating grooves (TM polarized).

4.6 Formation of multiple diffracted beams from a single laser beam by a 1D-DOE and arrangement for photoresist exposure.

4.7 Periodic near-field diffraction patterns created by (a) a single exposure with a 1D-DOE, (b) a single exposure with a similar 1D-DOE rotated by 90°, and (c) the resulting interlaced 3D woodpile structure due to combination of the two exposures in (a) and (b) with shift $S = c/4$ between two exposures.
4.8 Phasemask arrangement defining a two-dimensional DOE and providing adjustable separation, \(d\), for phase shift control of near-field diffraction patterns.

4.9 The 3D structure representations of DOE near-field diffraction patterns generated by interlacing of two 2D log structures: (a) BCT symmetry structure for \(S = 0\), and (b) diamond-like woodpile structure with TTR symmetry for \(S = c/4\).

4.10 Time averaged intensity profiles calculated by FDTD for a constant \(z = z_o\) plane, for increasing phasemask air gap \((\text{gap} = 1)\) of (a) \(d = 0.9084 \, \mu m\), \(S = c/4\), (b) \(d = 1.816 \, \mu m\), \(S = c/2\) (or 0), (c) \(d = 2.725 \, \mu m\), \(S = 3c/4\) (or \(c/4\)), and (d) \(d = 3.634 \, \mu m\), \(S = c\) (or 0). Here, \(a = \Lambda = 1.066 \, \mu m\).

4.11 (a) A two-level 2D DOE having groove depth of \(d\) and equal periodicities of \(\Lambda_x = \Lambda_y = \Lambda\). (b) One typical laser 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 \(n_s\).

4.12 A three-level DOE (a) color-coded for each phase level as defined by orthogonal grooves of periodicities \(\Lambda_x\) and \(\Lambda_y\), 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 \(n_s\).
4.13 Diffraction efficiency of a three-level DOE (Fig. 4.12a) as a function of groove depth $d_1$ with a fixed groove difference $(d_2 - d_1) = 331$ nm for diamond-like structure. Inset (i) shows the unit cell with $d_2$ and $d_1$ phase elements of refractive index, $n_d = 1.6$, in air background ($n_b = 1.0$) and substrate refractive index $n_s = 1.46$. \\

4.14 Near-field iso-intensity distribution computed by FDTD showing a single basis BCT symmetry structure as expected from the two-level DOE of $\Lambda = 570$ nm, $d = 0.565 \mu m$, $n_d = 1.46$. Inset (b) and (c) shows 2D intensity distribution ($<I(x, y)>$) of two planes clearly shows the BCT symmetry of the single basis structure. \\

4.15 Near-field iso-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 $\Lambda = 650$ nm, $d_1 = 1.13 \mu m$, $d_2 = 1.46 \mu m$, $n_d = 1.6$ and $n_b = 1.0$. Inset (b) and (c) shows 2D intensity distribution ($<I(x, y)>$) of two planes separated axially by $S = c/4 = 615$ nm distance which show orthogonally rotated log like intensity distributions as expected for a woodpile structure. \\

5.1 Beam delivery system. $M_n =$ turning mirrors, $A_n =$ alignment apertures, HWP = half waveplate, QWP = quarter waveplate, SF = spatial filter assembly consists of objective lens of NA = 0.1 and gold plated pinhole of diameter = 10 $\mu m$, $L_1 =$ collimating lens, BE = beam expander, $A_b =$ exposure beam size selecting aperture, ES = electronic shutter, VP = vacuum pump.
5.2 The photograph of the actual experimental beam delivery system. Important components have been labeled. 91

5.3 Argon ion beam profile (a)-(b) before mirror $M_1$, (c)-(d) after aperture $A_7$ and (e)-(f) after aperture $A_b$ as depicted in Fig. 5.1. 92

5.4 Absorption of H-Nu photoinitiators. 93

6.1 Double laser exposure based diamond-like woodpile photonic crystal fabrication technique. 99

6.2 Top SEM view (a) of the DOE fabricated 3D photonic crystal template together with cross-sectional view (b), showing 9 layers in the SU-8 photoresist. Inset (ii) shows magnified version of cross-section and inset (i) and inset (iii) shows interference equation based iso-intensity surface predictions. 100

6.3 Laser exposure setup of back to back connected two 1D-DOE forming a phase tunable DOE. 103

6.4 Top (a) and cross-sectional (b) SEM images of diamond-like woodpile structure with TTR symmetry fabricated using phase-tunable DOE method together with insets (i) and (ii), respectively, of matching iso-intensity surfaces computed by FDTD for $d = 2.725 \mu m$ and corresponding to $S = c/4$. 104

6.5 Top (a) and cross-sectional (b) SEM images of structure with BCT symmetry fabricated using phase-tunable DOE method together with insets (i) and (ii), respectively, of matching iso-intensity surfaces computed by FDTD for $d = 3.634 \mu m$ and corresponding to $S = c$. 105

xx
6.6 Top (a) and cross-sectional (b) SEM images of diamond-like woodpile structures having TTR symmetry together with insets (i) and (ii), respectively, of corresponding intensity distribution $\langle I(x,y) \rangle$ computed by FDTD for $d = 2.725 \, \mu m$ air gap between two phasemasks corresponding to shift $S = c/4$. 106

6.7 Band calculation (a) for double exposure formed woodpile template ($f = 64\%$, $c/a = 5.97$, $n_r= 1.6$) shown in Fig. 6.2 and (b) infrared spectral recording along $\Gamma-Z$ direction. (c) The Brillouin zone of the tetragonal lattice displaying scan path used in band calculation of (a) [22]. 109

6.8 Telecom-band transmission spectra through a woodpile template (Fig. 6.2) for various angles of incidence (degree) from the sample normal. 111

7.1 Atomic force microscope image of the two-level DOE of period $\Lambda_x = \Lambda_y = 570 \, nm$ and etch depth $d_t = 595 \, nm$. Inset (i) show single-line height profile that define groove depths $d_t$ (Length of scale bars as indicated). 116

7.2 Atomic force microscope image of the three-level DOE represented by the three different colors (heights). Enlarged section identifies a unit cell abcd (iii) and the ideal height profile ABCD (iv) used in the FDTD simulation. Inset (i) and (ii) show single-line height profiles in orthogonal scan directions that define groove depths $d_2$ and $d_1$ (Length of scale bars as indicated). 118

7.3 Laser exposure arrangement of a (a) two-level DOE and (b) the proposed three-level DOE 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 $n_a$. 119
7.4 Top (a) and cross-sectional (c) SEM images of the BCT symmetry structure in SU-8 photoresist. Inset-(iii) and (iv) shows enlarged views of top and cross-section. Inset-(i) and (ii) shows corresponding predicted near-filed isointensity surfaces computed by FDTD.

7.5 Top (a) and manually cleaved cross-sectional (b) SEM images of diamond-like woodpile structure in SU-8 photoresist showing 40 layers together with insets (i) and (iii), respectively, of predicted near-filed isointensity surfaces computed by FDTD. Inset (iv) shows enlarged view of cross-section of the actual structure and inset (ii) shows corresponding enlarged view of predicted isointensity surface of inset (iii) [36].

7.6 Band diagram (a) of the structure shown in Fig. 7.5 revealing a Γ-Z direction (normal incidence) (c-axis) stopband between the 5th and 6th band and corresponding normalized transmission spectrum (b) measured as normal angle of incidence through the structure in Fig. 7.5b showing a strong (-30 dB) stopband at 1.306 µm.

8.1 Transmission recording of Γ-Z stopband of the woodpile structure shown in Fig. 7.5 of Chapter 7 during Ethanol immersion (t = 0+) and evaporation (t > 0+) and corresponding comparison with air-filled photonic crystal spectrum (t = 0-).
8.2 (a) Laser exposure setup for single laser exposure fabrication of 3D periodic structure and micro-fluidic channels using a combination of diffractive and amplitude mask and (b) an amplitude mask for preferential masking of diffracted light to define open channels. Two layers of index matching medium ($n_i$) have been used between DOE substrate ($n_s$) and amplitude mask ($n_{AM}$) and also between amplitude mask and photoresist ($n_r$) layer which is spun onto a substrate of refractive index $n_s$. ................................. 132

8.3 (a) Micro-fluidic channel inside 3D structure and (b) enlarged view of the embedded 3D photonic crystal structures. ................................. 133

8.4 Top (a) and cross-sectional (b) SEM images of SiO$_2$ coated BCT symmetry structure. (c) and (d) corresponding top and cross-sectional views after SiO$_2$ over-layer removal. (e) FIB milled cross-section after removal of SU-8 template and the corresponding enlarged cross-sectional view is shown in (f). EDX spectra (g) and material composition (h) showing $\sim$90% presence of SiO$_2$ in the inverted structure. ................................. 136

8.5 Normalized transmission spectrum measured as normal angle of incidence through the structure in Fig. 8.4e showing a strong (-28 dB) stopband at 1.296 $\mu$m. ................................. 137

9.1 The photograph of a large area uniform 3D sample with four different viewing angles (a)-(d). (e) top SEM view of the sample. ................................. 142

A.1 Interference of diffracted beams from a phasemask inside a medium of refractive index ($n_r$). ................................. 148
Published Work

Journal publications as first author


Conference proceedings as first author


List of Acronyms

1D: one dimensional
2D: two dimensional
3D: three dimensional
AFM: atomic force microscope
BCC: body centred cubic
BCT: body centred tetragonal
CVD: chemical vapor deposition
CW: continuous wave
DLW: direct laser writing
DOE: diffractive optical element
EDX: energy-dispersive X-ray spectroscopy
FCC: face centred cubic
FIB: focused ion beam
FTIR: fourier transform infrared spectrometer
FWHM: full width at half maximum
HEX: hexagonal
HL: holographic lithography
OSA: optical spectrum analyzer
PBG: photonic bandgap
PWE: plane wave expansion
RIE: reactive ion etching
SEM: scanning electron microscope
SL: semiconductor lithography
SU-8: negative photoresist from Microchem
TTR: tetragonal
UV: ultraviolet
WG: waveguide
WP: waveplate
Chapter 1

Introduction

Light has played a significant role in the advancement of science and technology. The advent of coherent light from the laser in the 1960s [1, 2] has triggered the new era of scientific exploration with light. Further desire to manipulate light to explore the fundamental limits has led to the proposal of the three-dimensional (3D) periodic structures or photonic crystals at the end of 1980s [3, 4]. The three dimensionally periodic materials are artificial media which possess the ability of molding electromagnetic waves without absorption in similar way as electronic crystals act on electron waves. These 3D periodic structures are becoming a powerful tool for the manipulation of photons to fabricate interesting optical devices like filters, lasers, resonators and splitters. Demonstrations of physically interesting phenomena, such as the suppression or enhancement of light emission, have been pursued from the initial stages of photonic crystal research. Recently, highly functional integrated photonic chips and the application of photonic bandgap properties to optical quantum information processing have also been demonstrated. The conceptual development of 3D photonic crystals had lead to the study of the two-dimensional (2D) photonic crystals at the end of 1991 [5, 6]. A 2D photonic crystal is characterized by a two dimensional periodicity in the xy plane and by translational invariance along the z direction. This clearly indicates that light can propagate freely along
the z direction and as a consequence the most important property of a 3D photonic crystal, namely, light confinement along all \(4\pi\) directions or a complete bandgap, is not available in 2D case. Hence, for complete control of light, 3D photonic crystals are required. Apart from optical applications, these porous 3D periodic structures are also attractive as an artificially structured scaffold for biological and chemical applications. However, nano-scale fabrication of such complex artificial periodic structures pose a huge technological challenge. This has opened up vast opportunities for researchers to explore new 3D nanostructure fabrication techniques.

1.1 Motivation

For practical applications of three-dimensional nano-scale periodic structures, one needs to develop simpler and lower cost mass fabrication techniques of high precision. Unlike, two-dimensional planer structures, large-scale fabrication of 3D periodic structures using standard semiconductor lithographic technology is extremely tedious and costly due to repeated fabrication of multiple layers in the z direction [7, 8]. Even a flexible fabrication approach like laser direct writing where a tightly focused laser beam is used for photo-polymerization of 3D structures inside photo-sensitive materials becomes unacceptably time consuming for industrial batch fabrication even when processing sample sizes of only 100 x 100 microns [9, 10]. Colloidal self-assembly is limited to only face-centred-cubic (FCC) symmetry structure and is highly susceptible to stacking faults of the self-assembled spheres [11]. Holographic lithography (HL) based on interference of multiple laser beams has, in part, met these criteria by providing a large variety of photonic crystal templates in photo-sensitive materials [12]. 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 and also lead to uncontrolled symmetry due to random phase relation between interfering beams, making reproducibility an extreme challenge. In this context there is a promising alternative diffractive optics approach for creating multiple interfering laser beams in various diffraction orders from a single laser beam incident on a diffractive optical element (DOE). The multiple beams are inherently phase-locked to provide stable 3D near-field diffraction patterns without the instability problems of multi-beam HL. The concept behind 3D near-field diffraction pattern is well known since mid eighteen hundreds [13]. Rogers and coworkers [14] were first to demonstrate the formation of 3D periodic structures in photoresist using conformal phasemask DOEs. Lin et al. extended DOEs to the fabrication of 3D “Woodpile”-type photonic crystal templates in photoresist by double exposures of orthogonal phasemasks or one-dimensional DOEs (1D-DOE) [15]. However, imprecise alignment between two DOE exposures prevents this method from reproducibly generate 3D structures and a single exposure DOE method is therefore preferred for convenience and improved uniformity of the 3D structure. Further, 3D structures with smaller lattice constants are required for optical response in telecom band.

The biggest motivation of the present work is to design functional diffractive optics which will simplify 3D fabrication to a single laser beam and single optical element based approach where 3D crystal symmetry, lattice constants and basis information are encoded in the diffractive element design. Further, design of multi-level diffractive optical elements will allow one to manipulate the relative phase of diffracted beams to create complex near-field diffraction patterns. Special attention will be given to create diamond-like near-field intensity distribution due to its wide complete bandgap. Such near-field diffraction patterns will be captured
inside photosensitive materials to provide 3D photonic crystals of low refractive index contrast which will offer partial stopgaps along few preferential crystallographic directions. One objective will be to reduce axial to lateral crystal axis ratio \( (c/a) \) so that stopbands shift into the 1.25-1.65 \( \mu \text{m} \) telecom band. In principle, a complete photonic bandgap can be achieved by using a high refractive index photoresist or inverting these low refractive index templates with high refractive index materials [16].

1.2 New contributions

The main objective of this dissertation is to advance the diffractive optics based lithography technique to fabricate a wide range of three-dimensional periodic nanostructures. The complete process involved theoretical development, design, computation, modeling and fabrication. In this process, new contributions were made in several areas.

Photonic band calculation played an important role in predicting bandgap locations of 3D periodic structures. Isointensity surfaces were calculated from the design of diffractive optics which was followed with bandgap calculations to optimize the bandgap properties of the expected 3D templates both in photoresist and after inversion in silicon. A numerical band calculation code was developed as part of the present research work. Novel digital filtering techniques were implemented in the numerical band calculation algorithm to improve band calculation accuracy and reduce computation time enormously by approximately 1000 times which accelerated the progress of this research work.

For selecting a exposure laser and DOE period, the relation between crystal lattice constants with exposure laser wavelength and DOE period has been established. Detailed design criteria of all four proposed diffractive optics methods have been presented which were
supported with finite difference time domain (FDTD) prediction of near-field intensity distributions and numerical band calculation of expected band dispersion relations.

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. To overcome the inherently imprecise DOE alignment that arises between two laser exposures, 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.

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 ($\pi /2$ to $0$ radian) of one set of first order diffracted beams.

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 quarter period shift between two orthogonal interference patterns required for diamond-like woodpile structure. To improve fabrication reproducibility of diamond-like structure, a single-surface multi-level DOE device with an appropriate fixed phase-shift optimized for formation of diamond-like photonic crystal structure in a single laser exposure step was proposed. Finite difference time domain (FDTD) calculation of near-field diffraction patterns were corroborated by definitive demonstrations of diamond-like woodpile structure inside the photoresist as predicted.

This new multi-level DOE was fabricated and tested experimentally, permitting a large
number of layers (> 40) to form in thick photoresist. A record strength -30 dB stopband at 1.306 µm telecom band was observed. The usefulness of this stopband for refractive index sensing of liquids has been demonstrated. These low refractive index polymer structures were inverted with amorphous silica to convert a “soft” polymer structure to a robust structure made with a “hard” material. The high quality silica inverted structure promises possible use in biological sensing applications and also serves well for possible silicon double inversion for fabricating silicon 3D photonic crystals with a complete bandgap.

1.3 Overview of the dissertation

The dissertation is comprised of theoretical and experimental works and have been divided into separate chapters as follows:

In Chapter 2, the origin of three-dimensional periodic structure is reviewed. The theory behind the photonic bandgap has been discussed briefly. Different micro and nano fabrication techniques of 3D periodic structures have been described with merits and de-merits of each method is discussed.

In Chapter 3, the theoretical foundation of the present research work has been laid out. The under-lying physics behind diffractive optics lithography has been discussed in terms of Talbot self-imaging phenomenon. The beam walk-off has been characterized to define a practical working depth of near-field lithography. Effects of relative diffraction efficiency and laser polarization on near-field intensity distribution have been assessed with finite difference time domain (FDTD) calculations. The theory behind photonic band calculation has been discussed. Details of numerical band calculation have been elaborated with example band calculations.
In Chapter 4, the objective to create a diamond-like woodpile structure has been described. The band diagram of an optimized woodpile structure is presented and corresponding variation of the width of the complete bandgap with laser wavelength ($\lambda_d$) to the DOE period ($\Lambda$) ratio ($\lambda_d/\Lambda$) has been demonstrated. The theory and design guidelines of three proposed diffractive optic approaches for fabricating woodpile structure have been presented. The design started with 1D diffractive optics and then moved towards binary and then multi-level 2D diffractive optics to improve fabrication precision of 3D structures. Finite difference time domain calculation of near-field diffraction patterns and associated iso-intensity surfaces have been presented to corroborate definitive demonstration of a diamond-like woodpile structure formed inside photoresist.

In Chapter 5, the experimental fabrication and characterization techniques of 3D nanostructure are presented. The argon ion laser and beam delivery system for exposing photoresist has been described. The photoresist sample preparation, laser exposure procedures and structural and optical characterizations of 3D structures are presented.

In Chapter 6, results are presented for one-dimensional diffractive optics based double and single laser exposure fabrication of 3D structures. A novel phase control method has been demonstrated in generating a range of 3D structures, with symmetries from tetragonal (TTR) through to body-centred-tetragonal (BCT), that offer flexible tailoring of bandgap strength, width and spectral dispersion. A relatively long period DOE ($\Lambda = 1.066 \mu m$) provided 3D templates in SU-8 photoresist that confirm formation of thick, large area periodic nanostructures with optical response in the near-infrared band.

In Chapter 7, a novel single laser exposure method of fabricating diamond-like photonic crystals by multi-level diffractive optics has been presented. A short-period three-level DOE
(Λ = 650 nm) was laser-fabricated and applied to form 3D periodic structures in photoresist that confirm formation of thick, large area diamond-like nanostructures closely matching iso-intensity predictions of finite difference time domain computation. Spectroscopic characterization of the polymer structure revealed a strong stopband along the Γ-Z direction in the telecom band that was consistent with calculated band dispersion curves for the low-index medium.

In Chapter 8, application of strong and narrow stopgaps of polymer 3D photonic crystals in optical sensing has been demonstrated. A shadow masking technique has been demonstrated to integrate these 3D structures with micro-fluidic channels. As a final step, the polymer structures have been effectively inverted with silica using a chemical vapor deposition technique. The high quality silica inverted structure promises possible use of inverted structures in biological sensing applications as well as possible silicon double inversion for fabricating silicon 3D photonic crystals.

Finally, Chapter 9 concludes the thesis by summarizing the key findings and comparing the different 3D fabrication techniques. An outlook on future research directions have been outlined.
Chapter 2

Background on three-dimensional periodic structures

Three-dimensional periodic structures are unique in many ways. They form a porous medium which is attractive as an artificial structured environment for fundamental and applied physics studies. From a wave propagation point of view, the band dispersion relation of such media possess gaps in the k-space, unlike bulk materials, creating new opportunities in electromagnetic wave manipulations.

2.1 Brief history of photonic bandgap concept

The phenomenon of coherent back scattering was well known for a long time. Lord Rayleigh conjectured in 1887 that any arbitrary periodic arrangement of transparent materials will induce coherent back scattering for a band of frequencies for a specific angle of incidence [17]. This coherent back scattering or partial stopgap of one-dimensional (1D) periodic structures is known as Bragg reflection. However, the concept behind a complete photonic bandgap was proposed independently and simultaneously in 1987 by two researchers, each following a different path. Sajeev John was formulating a solution to the fundamental science question of whether photons can be trapped inside a strongly scattering medium like
electrons localization inside a disordered media and subsequently proposed that photons can be localized inside an appropriate arrangement of strong scatterers [4]. At the same time Eli Yablonovitch was trying to address some of the limitations of semiconductor lasers in terms of suppression of spontaneous emission [3]. He proposed that the spontaneous emission is not a fundamental property of matter but rather a characteristic of the coupling between electromagnetic waves and matter and can be controlled by placing the matter inside an artificially arranged environment. In confluence of these two lines of thoughts the complete photonic bandgap concept was born.

Following many unsuccessful trials, Yablonovitch finally proposed in 1989 a face-centred-cubic dielectric structure having a complete photonic bandgap [18]. Unfortunately, later theoretical studies [19] by full vectorial treatment of the Maxwell equations showed that the structure reported in [18] can not open a complete photonic bandgap. In between, Ho, Chan and Soukoulis showed that a diamond photonic crystal structure does have a complete photonic bandgap [20]. This was a very encouraging result which also proved that symmetry or lack of symmetry of the photonic crystal plays an important role in the formation of the photonic band structure. At the end of 1991, Yablonovitch, Gmitter and Leung created the first photonic crystal exhibiting a full photonic bandgap at microwave frequencies [21]. The proposed structure is famously known as Yablonovite, named after the inventor Yablonovitch, and shown in Fig. 2.1. The structure had been fabricated by drilling 3 pores oriented at 35.26° angle relative to the normal to the surface and with an azimuthal orientation at each point of 2D triangular lattice patterned surface of a solid slab of dielectric constant $\epsilon_{\text{background}} = 11.9$ as described in [21]. Following this seminal work, a wide range of 3D photonic crystal structures have been proposed and fabricated over the
Figure 2.1: Optimized Yablonovite structure. The crystal is characterized by $\varepsilon_{\text{background}} = 11.9$ and $\varepsilon_{\text{pore}} = 1$. The radius of the pores is $r_{\text{pore}} = 0.332|a|_{\text{hex}}$ where $|a|_{\text{hex}}$ is the Hexagonal Bravais lattice lattice constant. The air volume fraction of the structure is $= 78\%$. Figure from [22].

past two decades [11, 22]. Due to rather unique features, PBG materials have attracted the worldwide attention of physicists, chemists, engineers and industrial labs. In early stages, the study of photonic bandgap materials was concentrated mainly on their ability to guide and control light for possible passive applications in integrated optics. Recently, they are being used as a novel environment for strong coupling between light and matter for the study of quantum mechanical interactions.

2.2 Bandgap theory

Although a 3D periodic structure like the one shown in Fig. 2.1 sliced along a certain plane does not look like a stack of slabs similar to a 1D Bragg stack, stopgap formation in a specific direction occurs by the same mechanism. The challenge is designing a 3D periodic material for which there is an overlap of all Bragg stopgaps taken along all possible propagation directions over $4\pi$ steradian solid angle. This exhaustive search for stopgaps in an infinite
k-space can be reduced by taking advantage of the symmetry of the periodic structure. It has been shown that it is sufficient to scan only the irreducible Brillouin zone of the periodic structure for that purpose. The key factors in the formation of the complete photonic bandgap are the ones which influence the frequency positions and the width of stopgaps. The shape of the Brillouin zone is important and it is easy to understand that a spherical shape is desirable for maximum likelihood of overlap of all stopgaps in different directions. As width of stopgap is directly proportional to refractive index contrast, a large refractive index contrast of at least $\geq 2$ is required inside the unit cell of the periodic structure for opening up complete bandgap [20].

The spatial periodicity, which characterizes all photonic crystals, is described by means of Bravais lattices in a formalism completely analogous to the one used in the description of electronic crystals [23]. A photonic crystal structure is completely characterized by the distribution of the dielectric forming basis on a point lattice. For a Bravais lattice with primitive vectors of $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$, the following equality holds true for all integers $n_1$, $n_2$ and $n_3$: $\epsilon(\vec{r}) = \epsilon(\vec{r} + n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3)$.

Generally the spatial distribution of the dielectric or basis inside the primitive unit cell can be as complex as we can imagine. Further, the choice of the lattice-basis pair is not unique. Nevertheless almost all the photonic crystals known today can be described easily in terms of simpler building blocks. As an example, the Yablonovite photonic crystal shown in Fig. 2.1 can be modeled as a Hexagonal (HEX) Bravais lattice. The Hexagonal primitive unit cell and corresponding Brillouin zone has been shown in Fig. 2.2. The primitive unit cell is characterized by primitive vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ and the corresponding reciprocal unit cell or Brillouin zone is characterized by reciprocal vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$. The six vertices of the
Hexagonal irreducible Brillouin zone has been labeled with Roman letters as shown in Fig. 2.2b.

The most important feature of a photonic crystal is its unique electromagnetic characteristics which is completely different from its bulk material optical properties. In order to find this unique fingerprint, one needs to solve the Maxwell’s equations inside the photonic crystal. The solution of the Maxwell’s equations is most effectively represented by an band dispersion diagram. As an example, the band diagram of the Yablonovite photonic crystal shown in Fig. 2.1 has been calculated by solving Maxwell’s equation using the plane wave expansion method [22] and the result is shown in Fig. 2.3. For the band calculation, the propagation vector, $K_b$ (Bloch vector), has been chosen along the high symmetry points on the irreducible Brillouin zone of the Hexagonal Bravais lattice (Fig. 2.2b) following a path $\Gamma \rightarrow A \rightarrow H \rightarrow K \rightarrow \Gamma \rightarrow A \rightarrow L \rightarrow M \rightarrow \Gamma \rightarrow M \rightarrow K \rightarrow \Gamma \rightarrow L \rightarrow H \rightarrow \Gamma$. For each scan segment, 21 discrete values of $K_b$ have been chosen and for each point the lowest 20
Figure 2.3: Band dispersion diagram of the Yablonovite photonic crystal shown in Fig. 2.1. A complete bandgap opens between bands 6 and 7, is centered at $|a|_{\text{hex}}/\lambda_{\text{vac}} = 0.39$ and has a width of 16.9%. The location of the symmetry points used in the irreducible Brillouin zone path is shown in Fig. 2.2b. Figure from [22].

frequencies ($a/\lambda$) have been calculated. This then led to a plot like the one shown in Fig. 2.3 [22].

This mode of representation of the dispersion relation in terms of the band diagram clearly indicates a full photonic bandgap when it exists. The location and size of various stopgaps can also be immediately inferred from such a plot. An interesting point is that the band diagram predictions are completely scalable with the lattice constants of the periodic structure such that the stopbands appear fixed in the dispersion curves due to the $a/\lambda$ scaling of photon energy.

2.3 Three-dimensional periodic structures of special interest

A crystal is defined by two parts - lattice and basis. The lattice is the periodic outer framework and the basis is the spatial distribution of the “atom” at each lattice site inside the
primitive unit cell. According to crystallography, any three-dimensionally periodic structure can be classified as one of 14 Bravais lattices [23]. However, for a given lattice, an infinite choice of basis sets makes an infinite number of possible lattice-basis combinations. A wide range of 3D photonic crystal structures have been proposed and fabricated over the past two decades and each has been given an name to identify an unique lattice-basis combination [11, 22]. Among them, diamond and diamond-like structures, which are 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 [20, 22, 24]. However, fabrication of diamond or diamond-like structures is challenging and tedious due to the double basis nature of their crystal geometry. The laser fabrication of these double basis structures is one of the core motivations of the present research work.

2.3.1 Diamond structure

The diamond structure can be viewed as a FCC lattice with a basis formed by two “atoms” separated by a segment parallel with the main diagonal of the conventional FCC unit cell as shown in Fig. 2.4a where spherical atoms are placed on the lattice and nearest order neighbors are joined by cylindrical rods. It is well known that vibrant colors of butterflies and many other creatures found in nature are often due to the presence of some kind of periodic structure on their body [25]. Recently, it has been discovered that the unique color of a Beetle is due the presence of diamond structure on their scale [26] as shown in Fig. 2.4b.

From the photonic bandgap point of view, the reduced symmetry of this two atoms basis of diamond structure is the key factor in the breaking of the unwanted crossing be-
Figure 2.4: (a) The diamond structure spherical atoms are placed on the lattice and nearest order neighbors are joined by cylindrical rods. Figure from [22]. (b)-(h) SEM images of diamond structure in Beetle scales. Figure from [26].

tween degenerate bands present in the FCC based photonic crystals previously studied by Yablonovitch [18]. A large complete photonic bandgap of almost 30% was reported to open in a diamond photonic crystal made from overlapping air spheres in a background material with an index of refraction of 3.6 [20]. A sizable (∼16%) bandgap opens in the case of solid spheres as well.

2.3.2 Diamond-like structure

Another structure which has received considerable attention in the photonic crystal community is the woodpile structure, which was proposed by Ho, Chan and Soukoulis [24]. A tetragonal lattice with a basis formed by four identical rectangular prisms forms a woodpile structure as shown in Fig. 2.5. Due to resemblance with the two sphere diamond basis, the woodpile structure is called “diamond-like”. The woodpile structure can exhibit a complete photonic bandgap of 18% between the second and the third band for a 30% silicon volume filling fraction.
Due to log-pile like stacking of rods, the woodpile structure is ideally suited for sequential layer-by-layer fabrication processes. This has been demonstrated both by semiconductor lithography as well as by laser direct writing [8, 9]. However, these sequential fabrication techniques are very slow and parallel fabrication of multiple layers is essential for any large scale fabrication of woodpile photonic crystals.

2.4 Nano fabrication of 3D periodic structures

While the manufacturing of most of 3D photonic crystal structures on millimeter scales is a more or less a straightforward operation, the nanometer scale fabrication for operation in the optical domain has proved to be a very challenging task. Here we briefly discuss several prominent 3D nanostructure fabrication techniques.

2.4.1 Semiconductor lithography

Micro and nano fabrication of two-dimensional photonic planer structures using electron-beam or UV lithography is a well known procedure inherited from the well established
Figure 2.6: Scheme (a) and SEM (b) of woodpile photonic crystals fabricated by the layer-by-layer approach. Figure from [8].

microelectronics industry. In principle, the simplest way to extend UV lithography to three dimensional structure fabrication is to use a layer-by-layer approach. In a first step, the surface of a wafer is processed by electron-beam or UV lithography to create a 2D periodic pattern. The pattern is subsequently transferred to the substrate by dry etching. The next layer is then added either by deposition and subsequent patterning of a dielectric film or by bonding two pieces of independently patterned wafers at temperatures of several hundreds degrees Celsius (“wafer fusion” method), followed by removal of one of the substrates [7, 8]. This procedure is repeated several times until the desired number of layers is reached. The woodpile photonic crystal structure is ideally suited for such a sequential layer-by-layer approach. Susumu Noda has pioneered such fabrication processes and demonstrated fabrication of high quality woodpile structures [8] as shown in Fig. 2.6. The woodpile structure shown in Fig. 2.6b was fabricated using the III–V direct bandgap semiconductors GaAs and InP having photonic bandgaps at telecommunication wavelengths.

In practice, three-dimensional photonic crystals fabricated by this layer-by-layer fabrication approach are severely limited by the complexity of the fabrication process to only a few
lattice constants in the vertical direction. Additionally, a high degree of accuracy is required to avoid offsets between different layers. It is immediately apparent that such a sequential process is highly time consuming, expensive, and technically very tedious.

2.4.2 Self-assembly

Colloidal self-assembly of silica or polystyrene spheres can be used to fabricate artificial opal photonic crystals via sedimentation techniques where suspended spheres sediment on the substrate kept inside the colloid forming two equivalent dense packings of spheres with face-centred-cubic (fcc) or hexagonal-closed-packing (hcp) arrangements. In principle, this technique allows for simple and inexpensive large-area opal template fabrication [27, 28]. However, a complete photonic bandgap is not achievable for both fcc and hcp opals even with the refractive index limit of $n \rightarrow \infty$ [11]. However, to generate a complete bandgap, opals must be inverted with a high refractive index material. It has been shown in Ref. [29] that such a silicon inverted opal possesses a complete bandgap of 4.5%. The inversion can be performed by infiltrating air voids of opal with high refractive index materials and subsequent removal of the original spheres by wet chemical etching or plasma etching for silica and polystyrene, respectively. Figure 2.7 shows SEM images of (a) silica opal and (b) Si inverted opal from Ref. [28]. The Si inverted opal has been shown to possess complete bandgap in the telecom band [28].

The success of generating a complete bandgap critically depends on the quality of the inverted opal templates. Commercially available off-the-shelf spheres have standard deviations in their diameter on the order of 5% or more. Further, self assembled spheres are prone towards stacking faults [11]. This introduces sufficient disorder to close the anticipated
The complete photonic bandgap in inverted structures. Lastly, self-assembly method is severely limited by only fcc/hcp lattice type, as well as by only spherical basis which dramatically limits the 3D structural versatility available to the photonics engineer.

2.4.3 Direct laser writing

Recently, a wide range of 3D structures have been fabricated through direct laser writing (DLW) based on multi-photon polymerization. In DLW, a photoresist is illuminated by laser light whose photon energy is insufficient to expose the photoresist by a one-photon absorption process. However, when this laser light is tightly focused into the resist, the light intensity inside a small volume element (“voxel”) enclosing the focus may become sufficiently high to exceed the polymerization threshold of the photoresist by multi-photon absorption. Post exposure development then solidifies the polymerized volume and dissolves the underexposed volume for negative photoresist. A positive photoresist will otherwise dissolves the exposed volume. By scanning the tightly focused focal point relative to the photoresist, in principle, any arbitrary three-dimensional connected structure consisting of these voxels can be written directly into the photoresist. It is evident that due to non-linear light-matter interactions, femtosecond lasers are best suited for this purpose. A large variety of different
structures has been fabricated using femtosecond laser DLW in different kinds of photoresist. Some high quality 3D structures with sufficiently small lattice constants for stopgaps at telecommunication wavelengths have been reported by Martin Wegener and Hiroaki Misawa groups [9, 10]. One such woodpile structure taken from Ref. [9] has been shown in Fig. 2.8. The DLW method was used in fabricating the complete woodpile structure with 40 layers and the massive wall that prevented structural distortions during polymerization. The main attraction of DLW is that it conceptually allows for the incorporation of any arbitrary complex shape defect inside a 3D periodic structure.

It has been demonstrated that direct laser writing is capable of delivering high-quality three-dimensional nanostructures in a versatile fashion. However, to achieve three-dimensional
photonic crystals with a complete bandgap, the refractive index of typical photoresists, such as SU-8 ($n = 1.6$), is too small. Thus, inversion of these polymer structures with a high refractive index materials is necessary following single or double inversion processes [16, 30, 31]. The biggest drawback of laser direct writing is the unacceptable processing time when processing even for small sample sizes of only 100 µm x 100 µm, precluding DLW as an industrial batch fabrication technique of 3D micro-nano structures.

2.4.4 Holographic lithography

The main idea behind holographic lithography is to expose a thick photoresist to a standing light wave pattern originating from the interference of multiple laser beams. A schematic of four beam interference setup for holographic lithography producing a 3D interference pattern in the beam overlap region is shown in Fig. 2.9a [22]. It has been theoretically demonstrated that any of the 14 Bravais lattices in three dimensions should be realizable via holographic lithography by choosing a proper set of propagation vectors [22]. The first 3D structure fabricated using this technique was reported in March 2000 by Campbell et al. [12]. Figure-2.9b shows the SEM of corresponding fabricated 3D structure [12]. Subsequently many other groups independently demonstrated fabrication of 3D periodic structures using holographic lithography [32–34].

Due to low refractive index of photoresist, templates made by HL need to be inverted with high refractive index materials like templates made with DLW. Holographic lithography is a fast and relatively inexpensive fabrication method which in principle can be used to generate a large variety of 3D structures. 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 making reproducibility an extreme challenge.

2.5 Limitations of present 3D fabrication techniques

For practical use of optical domain three-dimensional photonic crystals there should be simpler and lower cost mass fabrication techniques. Most contemporary three-dimensional fabrication techniques are tedious or incompatible for mass production. Unlike, two-dimensional planer structures, large-scale fabrication of 3D photonic crystals using standard semiconductor lithographic technology is extremely tedious and costly prompting development of other unconventional 3D fabrication techniques. Even a flexible fabrication approach like laser direct writing becomes unacceptably time consuming for industrial batch fabrication when processing sample sizes of only 100 x 100 microns. Self-assembly based simple 3D fabrication method is limited by only FCC lattice type and is highly susceptible to stacking faults of the self-assembled spheres. Holographic lithography based on interference of mul-
multiple laser beams has, in part, met these criteria by providing a large variety of photonic crystal templates in photo-sensitive materials. However, the inherent vibrational instability problem of multiple beam holographic lithography introduces significant phase and angle errors during the exposure that distort and blur the 3D structure, making reproducibility an extreme challenge.

In this context there is a need for development of some flexible 3D fabrication techniques for high volume fabrication of 3D micro-nano structures. A diffractive optical element (DOE) is a promising alternative device for 3D lithography where one DOE creates multiple laser beams in various diffraction orders that are inherently phase-locked and stable for reproducible creation of 3D near-field diffraction patterns from a single laser beam. In this DOE approach, control parameters such as grating period, duty cycle and laser wavelength determine the periodic crystal structure while etch depth, laser intensity, polarization and photoresist threshold define the filling fraction and motif that together enables a wide variety of 3D photonic crystal structures to be formed. The concept behind 3D near-field diffraction pattern is well known since mid eighteen hundreds [13]. Rogers and coworkers [14] were first to demonstrate the formation of 3D periodic structures in photoresist using two-level (binary) DOEs. However, they could only fabricate a single basis structure with body-centred-tetragonal (BCT) symmetry as can be seen in Fig. 2.10.

In our group, Lin et al. extended DOEs to the fabrication of 3D “Woodpile”-type photonic crystal templates in photoresist by double exposures of orthogonal phasemasks or one-dimensional DOEs (1D-DOE) [15]. However, imprecise alignment between two DOE exposures prevents this method from reproducibly interlace two 2D structures and a single exposure DOE method is therefore preferred for convenience and improved uniformity of the
Figure 2.10: Body-centred-tetragonal (BCT) symmetry structure fabricated using binary 2D DOE. Inset (a)-(c) shows top view and inset-(b)-(d) shows cross-sectional SEM views. Figure from [14].

3D structures.

Figure 2.11: Scanning electron microscope image woodpile-type photonic crystal recorded in the SU-8 photoresist (a) top view of the photonic structure and (b) cross-section view of the photonic structure. Figure from [15].

In this thesis, we demonstrate improved fabrication precision and the first spectral characterization of Woodpile-type photonic crystal templates formed by 1D-DOE based double laser exposure method. Subsequently, more complex multi-level DOEs have been proposed to fabricate diamond-like photonic crystal structures in a single laser exposure step. These DOEs simplify the 3D fabrication process to a single optical element based approach where crystal symmetry, lattice constants, crystal basis information are encoded in the DOE [35,36]. Finite difference time domain calculation of near-field diffraction patterns are corroborated
by definitive demonstrations of diamond-like woodpile structure inside the photoresist. Special attention was given to reduce axial to lateral crystal axis ratio ($c/a$) so that stopbands shift into the 1.25-1.65 $\mu$m telecom band.
Chapter 3

Three-dimensional diffractive optics lithography

3.1 Introduction

Diffractive optics lithography is based on the near-field self-imaging effect of a periodic diffractive optical element (DOE). When a plane wave is transmitted through a periodic diffractive structure, the resulting wave front propagates in such a way that the light field replicates the structure along the propagation direction at multiples of a certain defined distance, known as the Talbot length. The main objective of diffractive optics lithography is to capture this 3D light intensity distribution inside a photosensitive material to fabricate 3D periodic structures or photonic crystals. By suitable design of the diffractive optical element, the 3D spatial light intensity distribution can be controlled to obtain desire lattice constants, motif shapes and symmetry. The origins of this 3D light intensity distribution, the conditions necessary for it to occur and the control of light distribution to different patterns are the subject of this chapter.
3.2 Talbot self-imaging

The Talbot effect was discovered by its namesake, Henry Fox Talbot, in the mid eighteen hundreds [13]. He examined a coarsely ruled diffraction grating with a simple magnifying lens and noticed that the grating image would reappear in the near-field of the grating as he moved the glass out of focus. The Talbot effect was forgotten until it was rediscovered by Lord Rayleigh in 1881. Rayleigh explained that the replication of the light intensity distribution in the near-field after diffracting through a periodic structure along the propagation direction at planes \( z = q Z_T \) where \( q \) is an integer, as a natural consequence of Fresnel diffraction, and showed that the Talbot length \( Z_T \) is given by

\[
Z_T = \frac{2\Lambda^2}{\lambda_m} \tag{3.1}
\]

where \( \Lambda \) is the period of the grating, \( \lambda_m \) is the wavelength of the light in the diffracting medium and \( n_m \) is the refractive index of the diffracting medium which are related with incident free space wavelength (\( \lambda_d \)) by \( \lambda_m = \lambda_d/n_m \). The Talbot effect has since been observed from any kind of periodic amplitude or phase diffractive elements [37, 38]. Figure 3.1 shows such a formation of Talbot self-images behind a grating where light intensity replicates the grating profile at locations that are integer multiples of Talbot length (\( Z_T \)). Halfway between Talbot distance of \( z = (q + \frac{1}{2}) Z_T \), phase reversed Talbot images appear with half period lateral shift (\( \Lambda/2 \)) with respect to the grating. Phase reversed Talbot image differs with Talbot self-image only by opposite phase relation and hence both possess identical intensity distribution. Both will be treated equally in this dissertation and will be referred as Talbot self-imaged planes.
Figure 3.1: Locations of Talbot self-images behind a grating.

Interesting image formations also take place in certain fractional Talbot planes, located between the planes $z = (q + \frac{1}{2}) Z_T$ [37, 38]. This fractional Talbot imaging phenomenon has been used in some interesting optical array illumination applications. However, in this dissertation we will strictly restrict ourselves to Talbot self-images to fabricate 3D periodic structures.

3.3 Arranging Talbot self-images into a photonic crystal

The Talbot self-imaging phenomenon can be observed in both amplitude and phase diffractive elements. However, only phase diffractive elements are considered here due to advantages of no energy loss as well as the possibility of diffraction control with multiple phase levels. This formation of near-field periodic light intensity distribution behind a diffractive optical element looks attractive in fabricating photonic crystals. However, the challenge is to control the periodic light intensity distribution so that it follows specific lattice constants, symmetry
and motif shape.

3.3.1 One-dimensional vs. two-dimensional diffractive elements

An one-dimensional DOE creates 1D self-image of the grating which repeats along the optical axis to form a 2D periodic pattern. A 2D DOE creates a 2D pattern which repeats along the optical axis forming a 3D periodic intensity distribution. There are five distinct Bravais lattices [23] for 2D periodic structures. However, in the present context we will only consider the square lattice 2D DOE. Figure 3.2a shows the near-field diffraction patterns of a 1 D DOE forming a 2D log-like intensity distribution having lattice constants $a$ and $c$. In contrast, a 2D DOE creates a 3D periodic diffraction pattern having lattice constants $a$, $b$ and $c$ as shown in Fig. 3.2b. However, for the Talbot self-imaging the DOE must produce at least $0^{th}$ and $±1^{st}$ diffracted beams [39]. This translationally symmetric arrangement of periodic Talbot self-images can be classified as a Bravais lattice. The lattice constants can be tuned by controlling diffraction angles produced by the DOE. This periodic diffraction pattern can be accurately captured inside a thick ($≫ c$) negative photoresist of refractive index $n_r$ placed in the beam overlap region as shown in Fig. 3.2 and by applying a laser exposure that just exceed the photo-polymerization threshold of the photoresist. However, a bi-continuous 3D intensity distribution is required for fabrication of stable 3D structures which does not collapse after photoresist development. This depends on the inherent connectivity as well as lattice constants of the intensity distribution.

3.3.2 Defining lattice constants

It can be observed from Eq. 3.1 that for a given incident laser wavelength ($\lambda_d$) and photoresist medium ($n_r$), both lateral lattice constants $a$ and $b$ and the axial lattice constant $c$ of the
periodic intensity distribution can be controlled by suitable selection of DOE period ($\Lambda$). Here, we assume that the 2D DOE period has equal periodicities of $\Lambda_1 = \Lambda_2 = \Lambda$ resulting in lateral lattice constant $b = a$ which is a valid assumption for cubic or tetragonal crystal symmetry groups and cases where $b \neq a$ will be highlighted separately. A complete photonic bandgap of photonic crystal structures is available only in a narrow range of cubic ($c = a$) or near-cubic ($c \sim a$) axial-to-transverse periodicity ratios, $c/a$, that further depends on the refractive index of dielectric medium and the filling fraction [22, 24]. However, for fabrication of cubic or near cubic crystals the ratio of the DOE period $\Lambda$ and the laser wavelength in the medium $\lambda_m$ should be on the order of unity requiring large diffraction angles of diffracted beam according to Eq. 3.2.

$$n_m \sin \theta_m + n_d \sin \phi = \frac{m\lambda_d}{\Lambda}$$

(3.2)

where $\phi$ is angle of incidence, $n_d$ is refractive index of incident medium and $\theta_m$ is diffraction angle of $m$-th diffraction order.
Talbot self-imaging of periodic structures is well known to be a strictly paraxial phenomenon. It was shown that the Talbot length ($Z_T$) departs significantly from its classical form shown in Eq. 3.1 if the ratio of the grating period $\Lambda$ and the laser wavelength $\lambda_d$ is of the order of ten, or less [38]. Assuming that only the three central diffraction orders ($m = -1, 0, 1$) are propagating waves, i.e., $1 < \Lambda/\lambda_m \leq 2$, it has been demonstrated from rigorous electromagnetic theory in [38] that for normal angle of incidence ($\phi = 0$) the field is always self-imaging for a generalized Talbot length given by:

$$Z_{Tg} = \frac{\lambda_m}{1 - \sqrt{1 - (\lambda_m/\Lambda)^2}}$$  \hspace{1cm} (3.3)

This generalized Talbot self-imaging length has been derived from interference equations and the complete derivation has been given in Appendix-A.

In this present research works the quest for fabricating cubic or near-cubic photonic crystal lattices is far beyond the paraxial condition where only three central diffraction orders ($m = -1, 0, 1$) are propagating waves. Hence, throughout this dissertation we will be using the generalized Talbot length of Eq. 3.3 which reduces to classical Talbot length of Eq. 3.1 for paraxial case of $\Lambda/\lambda_m \gg 1$. A comparison of the classical and the generalized Talbot length is presented in Fig. 3.3 which shows the variation of the ratio $Z_{Tg}/Z_T$ as a function of normalized wavelength inside the photoresist medium ($\lambda_m/\Lambda$).

In this research work, a wavelength to period ratio of $0.5 < \lambda_m/\Lambda < 1$ which necessitates reassignment of axial lattice constant $c$ to generalized Talbot length ($Z_{Tg}$). The modified lattice constants are shown in Eq. 3.4.

$$a = \Lambda; \quad c = Z_{Tg} = \frac{\lambda_m}{1 - \sqrt{1 - (\lambda_m/\Lambda)^2}}$$  \hspace{1cm} (3.4)
3.4 Determining depth of near-field

Due to finite size of any practical diffractive element and the large diffraction angles targeted here, the length of beam overlap region or near-field is limited to an extremely short region close to the diffractive element. This has been termed the “walk-off” effect in Talbot interferometry [39, 40]. This is one of the drawbacks of using higher-order Talbot self-imaging planes where diffracted beams gradually emerge as independent far-field beams. Hence, an accurate estimation of this beam overlap region is essential in estimating appropriate photoresist thickness and number of layers.

Figure 3.4 shows a ray-optics picture of far-field diffracted beams emerging from a DOE. Except around the boundary of the beam overlap region, the ray-optics approach has been found to accurately predict the central beam overlap region [39, 40]. Ray-optics approach will be used here to establish a closed-form analytical formula to estimate this beam overlap region. The hashed area in Fig. 3.4 shows a gradual narrowing of the conical shaped beam overall region away from a grating DOE. Diffracted beams at two arbitrary distances of (a)
Figure 3.4: Ray-optics picture of diffracted beam walk-off where $\mathbf{K}_0$, $\mathbf{K}_{\pm 1}$ represent propagation vectors of $0^{th}$ and $\pm 1^{st}$ order diffracted beams respectively.

Figure 3.5: Gradual narrowing of beam overlap region due to beam “walk-off” of a grating shown in Fig. 3.4 at arbitrary distances of (a) $L_1$ and (b) $L_2$ from grating surface as shown in Fig. 3.4.

$L_1$ and (b) $L_2$ away from the grating has been shown in Fig. 3.5. Here we can clearly observe as we move away from the grating the beam overlap region reduces and gradually far-field diffracted beams emerge with no mutual overlap between them.

The beam overlap region or near-field volume depends on period of the diffractive element ($\Lambda$) as well as on laser wavelength inside the medium ($\lambda_m$). Figure 3.6 shows beam overlap regions of diffraction from normally illuminated ($\lambda_d = 514$ nm) (a) 1D-DOE or phasemask of period $\Lambda = 650$ nm and (b) 2D-DOE of period $\Lambda_x = \Lambda_y = \Lambda = 650$ nm where the 1D-DOE
created 3 diffracted beams of (0,0), (1,0), (-1,0) order and the 2D-DOE created 5 diffracted beams of (0,0), (1,0), (-1,0), (0,1), (0,-1) where (m, n) represents order of a diffracted beam. To estimate the beam overlap region it has been assumed that the DOE is normally illuminated with a flat-top beam of radius $R$. In Fig. 3.6, $W_x$ and $W_y$ represents two radii of beam overlap region along X and Y axis and $P$ represents beam walk-off length at a given distance from the DOE. Following the diffraction angle equation of Eq. (3.2) and Snell’s law, the beam walk off length is:

$$P = \sum_{m=1}^{N} L_m \tan(\sin^{-1}\left(\frac{\lambda_d}{n_m\Lambda}\right))$$  \hspace{1cm} (3.5)$$

where $L_m$ is propagation distance in each medium, $N$ represents number of different medium between DOE and the plane of observation and $n_m$ is the corresponding refractive index of each medium. The corresponding beam overlap radius is given by:

$$W = (R - P) \ ; \forall P \leq R \ ; \forall W = \min(W_x, W_y)$$ \hspace{1cm} (3.6)$$

The depth of near-field can be estimated using Eq. (3.5) and Eq. (3.6) for a given beam overlap radius ($W$) to incident beam radius ($R$) ratio of $r = W/R$ inside a medium ($n_N$):
\[ d_{nf}(r, n_N) = \frac{(1 - r) R - \sum_{m=1}^{N-1} L_m \tan^{-1}\left(\frac{\lambda_d}{n_m A}\right)}{\tan^{-1}\left(\frac{\lambda_d}{n_N A}\right)}; \forall d_{nf}(r, n_N) \geq 0; \ 0 \leq r \leq 1; \quad (3.7) \]

where \(n_N\) is the refractive index of the recording medium where the near-field depth \(d_{nf}(r, n_N)\) is defined and \(n_1, ..., n_{N-1}\) and \(L_1, ..., L_{N-1}\) represent refractive indices and thicknesses of \((N - 1)\) media layers preceding the medium of observation \((n_N)\). According to Fig. 3.4 the near-field depth \(d_{nf}(r, n_r) = L_r\) inside the photoresist layer \((n_r)\) for a given beam overlap ratio of \(r = W/R = 0.5\). It can be guessed from Eq. 3.7 that to obtain a higher beam overlap ratio \((r = W/R)\) the laser wavelength to DOE period ratio \((\lambda_d/\Lambda)\) needs to be restricted to a lower value. However, as mentioned in Section 3.3.2 to achieve lower \(c/a\) ratio of the fabricated structure, laser wavelength to DOE period ratio \((\lambda_d/\Lambda)\) needs to be higher. This contradictory requirement requires special attention during DOE design.

### 3.5 Simulation of near-field intensity distribution

Simulation of the near-field diffraction pattern plays a key role in designing a diffractive optical element for 3D lithography. On one hand, the simulated intensity distribution helps in optimizing fabrication process and enables band calculation which in turn guides optical characterization of the fabricated structure. The band and intensity distribution calculation needs to be iteratively optimized for the final design of a diffractive optical element. The near-field diffraction pattern calculation starts with diffraction efficiency calculations and follows with interference intensity distribution and 3D isointensity surface generation.
3.5.1 Diffraction efficiency calculation

Diffraction efficiency of a DOE can be calculated by solving scalar or vector wave equations. However, in the present research where we always work in the non-paraxial regime ($\lambda \sim \Lambda$), full-vectorial calculation is required for accurate diffraction efficiency prediction [41]. There are two major full-vectorial diffraction efficiency calculation methods. One is Rigorous Coupled Wave Analysis (RCWA) [42] and another one is FDTD. However, it is well known that the RCWA predictions of diffraction efficiency is more accurate than FDTD predictions [41] and hence throughout this research work diffraction efficiency has been calculated using a RCWA based commercial algorithm GSolver (GSolver Inc.). The software uses a unit cell phase profile of a DOE to calculate diffraction efficiencies of different diffracted beams for a given laser wavelength, polarization and angle of incidence. The diffraction efficiency ($\eta_{mn}$) of $(m, n)^{th}$ diffraction order is defined by:

$$\eta_{mn} = \frac{P_{mn}}{P_{in}} = \frac{D_i D_i^*}{P_{in}}$$

(3.8)

where $P_{mn}$ is the power of $(m, n)^{th}$ diffraction order, $D_i$ is the corresponding amplitude of the diffraction order and $P_{in}$ is the incident power on the DOE. To illustrate calculation of diffraction efficiency, a 1D-DOE or phasemask of period $\Lambda = 650$ nm, DOE refractive index $n_d = 1.46$ and background refractive index $n_b = 1.0$ has been chosen for the arrangement Fig. 3.7. The mask has been illuminated normally with TM polarized laser light of wavelength $\lambda_d = 514$ nm where TM polarization is defined as polarization vector parallel to the grating grooves.

According to the diffraction angle equation Eq. (3.2), the DOE creates $(0, 0)$, $(1, 0)$ and $(-1, 0)$ order diffracted beams as shown in Fig. 3.7. The diffraction efficiency of $0^{th}$ and $1^{st}$
order beams of the DOE has been calculated using RCWA method and plotted in Fig. 3.8 as a function of DOE groove depth \(d_t\). The unit cell used in diffraction efficiency calculation has been shown in inset-(i) of Fig. 3.8. It can be observed that relative diffraction efficiency can be varied by varying DOE groove depth \(d_t\) for a given illumination conditions and refractive indices \(n_d\) and \(n_b\). The importance of relative diffraction efficiency will be discussed in Section 3.6.1.

### 3.5.2 Isointensity calculation

The near-field diffraction pattern can be generated in two different ways. In an approximate method the diffracted beams can be re-combined like far-field multiple beam interference to simulate near-field diffraction pattern. However, for more accurate finite difference time domain (FDTD) simulation, the laser light is propagated through the phase profile of a DOE to determine the intensity distribution in the near-field of the DOE. In our initial research
Figure 3.8: Diffraction efficiency of the 1D-DOE shown in Fig. 3.7 as a function of DOE groove depth \( d_t \) for DOE period \( \Lambda = 650 \) nm, DOE refractive index \( n_d = 1.46 \) and background refractive index \( n_b = 1.0 \). The DOE has been illuminated normally with TM polarized laser light of wavelength \( \lambda_d = 514 \) nm. Inset-(i) shows the unit cell used in diffraction efficiency calculation.

work we have used far-field interference for approximate predictions of near-field diffraction pattern and then moved to FDTD based exact near-field calculations for our later device demonstrations.

3.5.2.1 Interference equation based beam re-combination method

In diffractive optics lithography where the diffraction pattern is captured inside a photosensitive material using a step-function like response of the photo-sensitive material, less accurate far-field interference predictions have shown to match the contours of fabricated structures inside photo-sensitive materials [14,43]. In far-field calculation, parabolic or spherical wavefronts of near-field diffracted beams is approximated with plane wave wavefronts and each diffracted beam is treated as an independent monochromatic plane wave. The interference of \( N \) such diffracted beams of frequency \( \omega \), propagation vector \( \overrightarrow{K} \), polarization
vector $\mathbf{z}_i$ and diffraction amplitude $D_i$ creates a field given by:

$$\mathbf{E}(\mathbf{r}, t) = e^{-j\omega t} \sum_{i=0}^{N-1} D_i \mathbf{z}_i e^{j(K_i \cdot \mathbf{r} + \phi_i)}$$  \hspace{1cm} (3.9)$$

where the propagation vector $K_i$ is defined by diffraction angle and laser wavelength and $\phi_i$ is relative phase of diffracted beams. The diffraction amplitude $D_i$ is related to the incident power ($P_{in}$) through the diffraction efficiency ($\eta_{mn}$) as given in Eq. (3.8). The stationary intensity pattern produced by the interference described above is given by:

$$I(\mathbf{r}) = \mathbf{E}^*(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t) = \sum_{i=0}^{N-1} D_i^2 + 2 \sum_{i=1}^{N-1} D_0 D_i \mathbf{z}_0 \cdot \mathbf{z}_i \cos((K_i - K_0) \cdot \mathbf{r} + (\phi_i - \phi_0))$$  \hspace{1cm} (3.10)$$

$$+ \sum_{i>j=1}^{N-1} D_i D_j \mathbf{z}_i \cdot \mathbf{z}_j \cos((K_i - K_j) \cdot \mathbf{r} + (\phi_i - \phi_j)) = I_0 + 2 \Delta I(\mathbf{r})$$

where $I_0$ is the average background intensity and $\Delta I$ is the position dependent variation of intensity. The calculated intensity distribution is passed through a step-function threshold ($I_{th}$) to closely mimic the photoresist response, yielding the 3D isointensity distribution. By convention we consider that the high intensity regions in Eq. (3.10) will become the high dielectric component of the photonic crystal ($\epsilon(\mathbf{r}) = 1$ where $I(\mathbf{r}) < I_{th}$ and $\epsilon(\mathbf{r}) > 1$ where $I(\mathbf{r}) \geq I_{th}$).

### 3.5.2.2 Finite difference time domain method

The complex near-field diffraction pattern has been extensively studied by many researchers using scalar diffraction theory [44]. The scalar diffraction theory possesses closed form analytical expression and hence is relatively simple to use in predicting near-field diffraction patterns. Unlike scalar theory, there is no closed form analytical expression for calculating near-field diffraction with a full vectorial approach. Hence, one needs discrete numerical
approaches like finite difference time domain (FDTD) computations to accurately simulate
diffraction patterns.

The near-field intensity distribution \(< I(x, y, z) >\) of the 1D-DOE shown in Fig. 3.7 has been calculated using Lumerical-FDTD (Lumerical Inc.). For this FDTD calculation, according to Fig. 3.8 DOE groove depth of \(d_t = 0.5 \ \mu m\) was chosen for equal diffraction efficiency of \(0^{th}\) order and \(1^{st}\) order beams \((\eta_{00} = \eta_{10} = \eta_{-10} = 32.7 \%)\). The TM polarized plane wave light of \(\lambda_d = 514 \ \text{nm}\) was propagated through the above 1D DOE of period \(\Lambda = 650 \ \text{nm}\), groove depth \(d_t = 0.5 \ \mu m\), DOE refractive index \(n_d = 1.46\) and background refractive index \(n_b = 1.0\) as arranged in Fig. 3.7. The calculated near-field intensity distribution was passed through a step-function threshold yielding the 3D isointensity distribution as shown in Fig. 3.9. From Fig. 3.9 it can be observed that log-like self-image of the 1D-DOE repeats along the optical axis (z-direction) as expected from the discussion of Section 3.2.

3.6 Controlling near-field intensity distribution

In 3D diffractive optics lithography, the overall intensity distribution closely replicates the pattern of the original diffractive structure. However intensity contrast, uniformity and feature sizes of the intensity distribution depend on the relative diffraction efficiencies of diffraction orders and the polarization of incident laser beam. Further, the relative phase of the diffracted beams can alter the intensity distribution.

3.6.1 Effect of diffraction efficiency

For 3D lithographic a high contrast \((\Delta I \gg I_0)\) and uniform 3D near-field intensity distribution is highly desirable. This immensely facilitates in obtaining an optimum laser exposure dose
Figure 3.9: FDTD calculation of isointensity surface of the near-field diffraction pattern of the 1D-DOE shown in Fig. 3.7 for normal incident TM polarized plane wave light of wavelength $\lambda_d = 514$ nm.

as well as a wider exposure window to optimize filling fraction ($ff$) of the 3D structure. The intensity contrast is defined as:

$$C = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \quad (3.11)$$

From Eq. (3.9) it is evident that the intensity contrast depends on relative amplitudes ($D_i$) of the diffracted beams (i.e. diffraction efficiency). To illustrate the inter relation between intensity contrast and relative diffraction efficiency, a near-field diffraction pattern of the DOE shown in Fig. 3.7 has been calculated using FDTD for same set of parameters used in the diffraction efficiency calculation in Fig. 3.8. A TM polarized plane wave light of wavelength $\lambda_d = 514$ nm has been propagated through the 1D-DOE shown in Fig. 3.7 for varying groove depth $d_i$ between the range 0.47 $ \mu m$ - 0.1 $ \mu m$, which according to Fig.
3.8 corresponds to the range of $0^{th}$ to $1^{st}$ order diffraction efficiency ratio of $\eta_0/\eta_1 = 0.58 - 20$ for constant DOE refractive index $n_d = 1.46$ and background refractive index $n_b = 1.0$. The variation of intensity contrast ($C$) with the diffraction efficiency ratio ($\eta_0/\eta_1$) is shown in Fig. 3.10. It can be observed from Fig. 3.10 that the intensity contrast is insensitive to relative diffraction efficiency of $0^{th}$ order and $1^{st}$ order diffracted beams for a relatively large diffraction efficiency ratio of $\eta_0/\eta_1 \approx 1$ to 6 which means each of $\pm 1^{st}$ order beams should possess at least $\approx 12.5\%$ diffraction efficiency in order to maintain maximum intensity contrast of $C = 1$. This point highlights the importance of accurate diffraction efficiency estimation in DOE design for creating high contrast intensity distribution. This is essential in diffractive optics lithography for precise control of laser exposure dose to obtain a structure with a desired filling fraction.

### 3.6.2 Effect of polarization

Diffraction efficiency of a phase only diffractive structure primarily depends on phase depth. It is generally believed that diffraction efficiency doesn’t depend on polarization of incident light. However, for non-paraxial case ($\Lambda \sim \lambda$) it has been found that diffraction efficiency is also a function of polarization of incident light [38].

#### 3.6.2.1 Effect on diffraction efficiency and intensity contrast

To understand the effect of polarization, the diffraction efficiency of the same 1D-DOE or phasemask shown in Fig. 3.7 has been calculated for TE, TM and circularly polarized light by the RCWA method. The same DOE parameters of period $\Lambda = 650$ nm, DOE refractive index $n_d = 1.46$, background refractive index $n_b = 1.0$ and laser wavelength of $\lambda_d = 514$ nm have been used. The laser wavelength $\lambda_d = 514$ nm and phasemask period $\Lambda = 650$ nm
Figure 3.10: Variation of intensity contrast \((C)\) with 0\(^{th}\) order to 1\(^{st}\) order diffraction efficiency ratio \((\eta_0/\eta_1)\) of the near-field intensity distribution of the 1D-DOE shown in Fig. 3.7 for same set of parameters used in the diffraction efficiency calculation in Fig. 3.8. The diffraction efficiency ratio \(\eta_0/\eta_1 = 0.58 - 20\) of RCWA based diffraction efficiency prediction corresponds to DOE groove depth \(d_t\) between the range 0.47 \(\mu m\) - 0.1 \(\mu m\).

have been chosen specifically to satisfy the non-paraxial condition. Results for 0\(^{th}\) and 1\(^{st}\) order beams are shown in Fig. 3.11 as a function of DOE groove depth \(d_t\).

From Fig. 3.11 it can be observed that diffraction efficiency depends on polarization of the incident laser beam. For a given groove depth \((d_t)\) diffraction efficiency of TE and TM polarized light differs by up to 25\%. As expected, diffraction efficiency of circularly polarized light is halfway between that for TE and TM polarized light. The corresponding variation of intensity contrast \((C)\) with diffraction efficiency ratio \((\eta_0/\eta_1)\) is shown in Fig. 3.12 for all three polarizations. It can be observed that unlike TM polarization, intensity contrast strongly depends on \(\eta_0/\eta_1\) ratio for TE and circular polarizations. This shows the importance of polarization in obtaining desired diffraction efficiencies of a given DOE and
consequently a desired intensity contrast of a near-field intensity distribution.

3.6.2.2 Effect on motif shape

To illustrate the effect of polarization on feature size or motif shape, the intensity variation along a line passing through a maximum intensity point in the x and z directions of Fig. 3.9 has been shown in Fig. 3.13. For comparison purposes, the diffraction efficiency ratio, \( \eta_0/\eta_1 = 1 \) has been chosen for all three polarizations which according to Fig. 3.11 corresponds to DOE groove depths of \( d_t = 365 \) nm, 499 nm and 426 nm for TE, TM and circularly polarized normal incident laser light. The motif shape factor of the log-like intensity distribution of the 1D-DOE has been defined by relative ratio \( S_f = R_z/R_x \) between two radii along axial \((R_z)\) and lateral directions \((R_x)\). It can be observed from Fig. 3.13 that motif shape \( (S_f) \) strongly
Figure 3.12: Variation of intensity contrast ($C$) with the diffraction efficiency ratio ($\eta_0/\eta_1$) of the near-field intensity distribution of the 1D-DOE shown in Fig. 3.7 for same set of parameters used in the diffraction efficiency calculation in Fig. 3.11 for TE, TM and circularly polarized light.

depends on incident laser polarization. A motif shape factor of $S_f = 1.63, 4.7$ and 3 has been measured for TE, TM and circular polarization, respectively, from Fig. 3.13 using the calculated full-width-half-max (FWHM) widths of $R_z$ and $R_x$. It is interesting to observe that motif shape factor of circularly polarized light is more similar to TM polarized light than TE polarized light.

The relative motif shape for TE, TM and circularly polarized incident light has been shown in Fig. 3.14 corresponding to the above motif shape factors of $S_f = 1.63, 4.7, 3$. It can be observed that for TM polarization, motif shape is slim along the lateral direction and elongated in the axial direction compared to motif shape for TE polarization. Circular polarization demonstrates an interesting behavior where axial radius ($R_z$) is elongated without changing lateral radius ($R_x$) by much. Elongation of motif along axial direction ($R_z$) can be
Figure 3.13: Intensity variation across a line (a) in the x and (b) in the z directions of Fig. 3.9 passing through the maximum intensity point in the respective directions calculated by FDTD.

useful for establishing connection between two adjacent layers in the axial direction to form a stable interconnected 3D structure [43].

The motif shape factor plays an important role in controlling filling fraction with laser exposure dose. Figure 3.15 shows change of filling fraction with laser exposure dose of the same intensity distribution shown in Fig. 3.9. The laser exposure dose has been normalized with the maximum intensity of three intensity distributions corresponding to three polarizations. It can be observed from Fig. 3.15 that for a given laser exposure dose TE, TM and circular polarization creates intensity distribution with three different filling fractions. The slope of change of filling fraction curve dictates the sensitivity of laser exposure dose control in obtaining a given filling fraction for a given polarization. Hence, selecting a proper polarization for a given DOE design is very important for fabrication of high quality reproducible 3D structures.
3.6.3 Effect of relative phase of diffracted beams

It is evident from Eq. (3.10) that the interference pattern depends on the relative phase \( \phi_i \) of the interfering beams. Relative phase between interfering beams has been shown to change interference pattern by inserting delay elements in one or more beam paths in multi-beam interference [45]. Similar effects have been demonstrated in cross-grating based far-field interference as well [46]. However, unlike multi-beam holography, relative phase control of diffracted beams is not possible in near-field diffractive optic lithography. Since all diffracted beams are phase locked with respect to the diffracting surface.

In the present research work we propose a phase-tunable DOE with multiple surfaces which enabled tuning of phase difference of one set of first order diffracted beams with the physical separation between the two diffractive elements which enabled fabrication of continuum of different 3D periodic structures that are tunable from the double basis diamond-like structure to a single basis structure having body-centered-tetragonal symmetry (BCT). Fur-
Figure 3.15: Change of filling fraction as a function of exposure dose of the intensity distribution shown in Fig. 3.9.

Further, we propose a single-surface multi-level DOE with locked-in phase shift to enable fabrication of a wide range of 3D structures. These phase control mechanisms will be elaborated in subsequent chapters.

3.7 Photonic band calculation

Band calculation plays the most important part in characterizing any periodic structure. There are number of different techniques for band calculations of electronic crystals, however band structures of photonic crystals have almost exclusively been obtained from the plane wave expansion (PWE) method [20]. This is a well known concept of solving Maxwell’s equations for any spatially periodic structures. Unlike electronic crystals, the “periodic potentials” in photonic bandgap materials are known and do not need to be computed in a self-consistent fashions like electronic crystals.
3.7.1 Plane wave expansion theory

The PWE method is based on the Bloch-Floquet theorem, which states that Eigen solutions of differential equations with periodic coefficients may be expressed as a product of plane waves and lattice-periodic functions. Consequently, all periodic functions are expanded into appropriate Fourier series. Inserting these expansions into the Maxwell's equations results in a large matrix-eigenvalue problem, which after suitable truncation, provides the Eigen frequencies and expansion coefficients for the Eigen function [20].

We start with vector wave equations for displacement field, $\overline{D}$.

$$\nabla \times \nabla \times \frac{\overline{D}(\tau)}{\epsilon(\tau)} = \frac{\omega^2}{c^2} \overline{D}(\tau)$$  \hspace{1cm} (3.12)

The periodic dielectric constant defines a three-dimensional lattice and corresponding three-dimensional reciprocal lattice vectors defined by $\kappa(\tau) = 1/\epsilon(\tau)$. Using the Bloch theorem and Fourier expansion, $\overline{D}(\tau)$ and $\kappa(\tau)$ can be written as:

$$\overline{D}(\tau) = d(\tau) e^{i\kappa\tau} = \sum_{\mathcal{G}} d_{\mathcal{G}} e^{i\mathcal{G}\tau} e^{i\kappa\tau} = \sum_{\mathcal{G}} d_{\mathcal{G}} e^{i(\kappa+\mathcal{G})\tau}$$  \hspace{1cm} (3.13)

$$\kappa(\tau) = \sum_{\mathcal{G}} \kappa_{\mathcal{G}} e^{i\mathcal{G}\tau}$$  \hspace{1cm} (3.14)

where $\mathcal{G}$ is the reciprocal lattice vector of the periodic structure. By substituting Eq. (3.13) and Eq. (3.14) into Eq. (3.12), we get

$$\nabla \times \nabla \times \left( \sum_{\mathcal{G}_1, \mathcal{G}_2} \kappa_{\mathcal{G}_2} d_{\mathcal{G}_1} e^{i(\kappa+\mathcal{G}_1+\mathcal{G}_2)\tau} \right) = \frac{\omega^2}{c^2} \sum_{\mathcal{G}} d_{\mathcal{G}} e^{i(\kappa+\mathcal{G})\tau}$$  \hspace{1cm} (3.15)

The divergence-free electric field permits an expansion of the form
\[ D_k = \sum_{\lambda} \sum_{\mathcal{G}} w_{\mathcal{G}}^{\lambda} S_{\mathcal{G}}^{\lambda} e^{i(k + \mathcal{G})\mathbf{r}} \]  

(3.16)

where \( S_{\mathcal{G}}^{\lambda}, \lambda = 1, 2 \) denote two unit vectors such that the set \( \{ S_{\mathcal{G}}^{\lambda=1}, S_{\mathcal{G}}^{\lambda=2}, (k + \mathcal{G}) \} \) forms an orthogonal triad. The matrix-eigenvalue equation corresponding to Eq. (3.15) then becomes

\[ \sum_{\mathcal{G}} \sum_{\mathcal{G}'} \kappa_{\mathcal{G} - \mathcal{G}'} |k + \mathcal{G}||k + \mathcal{G}'| (S_{\mathcal{G}}^{\lambda=1}S_{\mathcal{G}'}^{\lambda=1} S_{\mathcal{G}}^{\lambda=2}S_{\mathcal{G}'}^{\lambda=2}) \begin{pmatrix} w_{\mathcal{G}}^{1} \\ w_{\mathcal{G}}^{2} \end{pmatrix} = \omega_{k}^{2} \begin{pmatrix} w_{\mathcal{G}}^{1} \\ w_{\mathcal{G}}^{2} \end{pmatrix} \]  

(3.17)

where \( \{ w_{\mathcal{G}}^{\lambda=1}, w_{\mathcal{G}}^{\lambda=2} \} \) are eigenvectors corresponding to the E or H field. Again, following Ref. [20], instead of computing the Fourier coefficients \( \kappa_{\mathcal{G} - \mathcal{G}'} \) directly from Eq. (3.14), we compute the matrix \( \epsilon_{\mathcal{G} - \mathcal{G}'} \) of Fourier coefficients of \( \epsilon(\mathbf{r}) \) for the set of reciprocal lattice vectors that define the matrix in Eq. (3.17). We then take \( \kappa_{\mathcal{G} - \mathcal{G}'} \) to be the \( (\mathcal{G}, \mathcal{G}') \) element of the inverse of the matrix \( \epsilon_{\mathcal{G} - \mathcal{G}'} \). This procedure is known to dramatically improve the convergence of eigenvalue computations [29, 47, 48]. Regular geometrical shapes like circle, rectangle, sphere and cylinder possess closed form analytical expression for Fourier coefficient \( \epsilon_{\mathcal{G} - \mathcal{G}'} \) and hence it is straightforward to solve Eq. (3.17) to obtain the band dispersion relation of structures made of these fundamental motifs. However, structure made of irregular motif does not possess a closed form expression for \( \epsilon_{\mathcal{G} - \mathcal{G}'} \) and hence need numerical techniques to solve Eq. (3.17) for such structures.

3.7.2 Numerical plane wave expansion of periodic structures

The periodic structures made of highly convoluted shapes that do not conform to any typically known regular geometrical shapes and therefore preclude the use of analytic approaches for the plane wave expansion method to accurately generate the band-dispersion curves. However, with numerical techniques, bands of any arbitrary shape periodic structure can be
computed accurately as discussed in this section.

3.7.2.1 Discrete representation and classification of the 3D periodic structures

For numerical band calculation, the isointensity surface computed following methods Section 3.5.2 is decomposed into a fine mesh grid where each grid point represents the relative permittivity of the material at that point. Selection of appropriate spatial sampling frequency of the 3-dimensional mesh is critical for the accuracy of the PWE method. Overly coarse meshing of the structure leads to significant aliasing errors in the band calculation. In some cases irregular motifs make it difficult to estimate the appropriate spatial frequency of the structure. In those cases aliasing errors can be avoided by selecting a large number of mesh points. However, structures with highly convoluted features also require low pass filtering to avoid sampling anomalies in numerical band calculation.

The observed structure is first classified amongst the 14 known Bravais lattices [23] in order to identify reciprocal lattice vectors ($\mathbf{G}$) which best represent the symmetry of the structure. Due to highly convoluted shapes of these structures, this classification process is cumbersome. Inspection of such a structure does not immediately reveal its symmetry and requires cross-sectional views of various planes to be plotted as mentioned in [49]. This principle of identifying the Bravais lattice symmetry can be extended to any 3D periodic structure which simply requires that appropriately spaced cross-sectional views be examined that reveal the structural periodicity along the x, y and z directions.

3.7.2.2 Numerical representation of plane wave expansion

To solve Eq. (3.17) numerically, reciprocal lattice vectors ($\mathbf{G}$), Fourier coefficients $\kappa_{\mathbf{G} - \mathbf{G}'}$ of the structure and orthogonal vectors {$S^{\lambda=1}_{\mathbf{G}}, S^{\lambda=2}_{\mathbf{G}}$} have to be obtained for each scan point
(\vec{k}) along the Brillouin zone of the Bravais lattice of the structure.

**A. Scanning along the irreducible Brillouin zone**

To solve the Eigen values of the matrix formed by Eq. (3.17), a \vec{k}-space needs to be selected over which the bandgap of the structure is probed. It is well known from semiconductor physics that to accomplish this purpose it is sufficient to choose \vec{k} from the irreducible Brillouin zone of the reciprocal structure [23]. Moreover, to save computation time, only scan paths along high symmetry points of the irreducible Brillouin zone can be probed for the band calculation because only at the boundaries of the Brillouin zone Bragg diffraction condition is satisfied which enhances the possibility of opening up of the bandgap at that point on the \vec{k}-space.

**B. Finding lattice constants of the discretized structure**

Both real and reciprocal lattice constants of a periodic structure should be known for plane wave expansion of the structure. If we assume that a 3-dimensional structure possesses \(P_x\) period in x-direction, \(P_y\) period in y-direction and \(P_z\) period in z-direction. Then the discrete domain lengths of the unit cell in x, y, z directions are \(a'_x = \frac{N_x}{P_x}\), \(a'_y = \frac{N_y}{P_y}\), \(a'_z = \frac{N_z}{P_z}\), where \(N_x\), \(N_y\) and \(N_z\) are the number of samples of the discrete structure in the x, y, z directions, respectively. Hence, normalized lengths of the unit cell in x, y, z directions are \(a_x = \frac{a'_x}{a}\), \(a_y = \frac{a'_y}{a}\), \(a_z = \frac{a'_z}{a}\) where \(a = \min\{a'_x, a'_y, a'_z\}\). Now depending on the particular lattice symmetry, primitive lattice constants of the real space are derived as function of \(a_x\), \(a_y\) and \(a_z\). For example, Tetragonal (TTR) primitive lattice constants are \(\vec{a}_1 = [a_x, 0, 0]\), \(\vec{a}_2 = [0, a_y, 0]\) and \(\vec{a}_3 = [0, 0, a_z]\). From primitive lattice constants of the real space, lattice constants for the reciprocal space can be obtained as:
\[
\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}, \quad \vec{b}_2 = 2\pi \frac{\vec{a}_1 \times \vec{a}_3}{\vec{a}_2 \cdot \vec{a}_1 \times \vec{a}_3}, \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2}
\] (3.18)

From the classification of the 3-dimensional periodic structure according to one of the 14 Bravais lattices, the primitive \( \{\vec{a}_1, \vec{a}_2, \vec{a}_3\} \) and reciprocal \( \{\vec{b}_1, \vec{b}_2, \vec{b}_3\} \) lattice constants are obtained as described above. The reciprocal lattice vectors \( \vec{G} \) are formed as \( \vec{G} = s_1\vec{b}_1 + s_2\vec{b}_2 + s_3\vec{b}_3 \) where \( s_1, s_2, s_3 \) are integers. In plane wave expansion method these \( \vec{G} \) are considered as plane waves. For accurate band calculation \( \vec{G} \) should span a symmetric 3-dimensional volume like a sphere or cube in the reciprocal space of the lattice. Ideally, an infinite number of plane waves \( \vec{G} \) are needed for accurate band calculation. However, for all practical purposes, the band diagram obtained with sufficiently large number of plane waves \( \vec{G} \) converge accurately. The dependence of band calculation accuracy on number of plane waves is shown in Section 3.7.3.1.

C. Finding orthogonal unit vectors

In Eq. (3.17), \( \vec{S}_{\lambda=1,2} \) denote two unit vectors such that the set \( \{\vec{S}_{\lambda=1}^{\vec{G}}, \vec{S}_{\lambda=2}^{\vec{G}}, (\vec{k} + \vec{G})\} \) forms an orthogonal triad. That means for each scan point \( \vec{k} \) and for each reciprocal lattice vector \( \vec{G} \), two mutually orthogonal unit vectors which are normal to \( \vec{k} + \vec{G} \), need to be defined. This can be accomplished as [50]:

\[
\vec{Z}_{\vec{k}+\vec{G}} = \frac{(\vec{k} + \vec{G})}{|\vec{k} + \vec{G}|}; \quad \vec{S}_{\lambda}^{\vec{G}} = \frac{(\vec{k} + \vec{G}) \times \vec{A}}{|(\vec{k} + \vec{G}) \times \vec{A}|}; \quad \vec{S}_{\lambda}^{\vec{G}} = \vec{Z}_{\vec{k}+\vec{G}} \times \vec{S}_{\lambda}^{\vec{G}}
\] (3.19)

where \( \vec{A} \) is an arbitrary vector which is not parallel to \( (\vec{k} + \vec{G}) \).
D. Fourier expansion of the discrete structure

To solve the eigenvalue Eq. (3.17), one requires the Fourier coefficients $\kappa_{\mathbf{G} - \mathbf{G}'}$. Again, as stated in Section 3.7.1, instead of computing the Fourier coefficients directly from Eq. (3.14), we compute the matrix $\epsilon_{\mathbf{G} - \mathbf{G}'}$ of Fourier coefficients of $\epsilon(\mathbf{r})$ for the set of reciprocal lattice vectors that define the matrix in Eq. (3.17). A fast Fourier transform is used as the mathematical tool to expand the 3-dimensional periodic structure ($\epsilon(x, y, z)$) in terms of plane waves.

$$\epsilon(f_x, f_y, f_z) = \sum_{m_x=0}^{N_x-1} \sum_{m_y=0}^{N_y-1} \sum_{m_z=0}^{N_z-1} \epsilon(x, y, z) e^{-i(\frac{2\pi}{N_x} m_x k_x + \frac{2\pi}{N_y} m_y k_y + \frac{2\pi}{N_z} m_z k_z)}$$

(3.20)

where $m_x = 0, 1, \ldots (N_x - 1)$, $m_y = 0, 1, \ldots (N_y - 1)$, $m_z = 0, 1, \ldots (N_z - 1)$ and $k_x = 0, 1, \ldots (N_x - 1)$, $k_y = 0, 1, \ldots (N_y - 1)$, $k_z = 0, 1, \ldots (N_z - 1)$. $N_x$, $N_y$, $N_z$ are lengths of the structure in x, y, z directions respectively. In the Fourier transform, the discrete plane wave frequency bins are:

$$f_x = \frac{2\pi}{N_x} k_x, f_y = \frac{2\pi}{N_y} k_y, f_z = \frac{2\pi}{N_z} k_z$$

(3.21)

The matrix $\epsilon(f_x, f_y, f_z)$ contains plane wave expansion coefficients for all frequency bins ranging between 0 to $\frac{2\pi}{N_s}(N_s - 1)$ for $s = x, y$ and $z$. However, to solve the eigenvalue Eq. (3.17), the PWE coefficients for frequency bins at previously specified reciprocal lattice vectors ($\mathbf{G} - \mathbf{G}'$) are needed. Hence, we need to establish a relation between $\epsilon(f_x, f_y, f_z)$ and $\epsilon(\mathbf{G} - \mathbf{G}')$. Careful observation reveals that

$$G_x - G'_x = \frac{2\pi}{a_x} a g_x, g_x \in \mathbb{R}; \quad G_y - G'_y = \frac{2\pi}{a_y} a g_y, g_y \in \mathbb{R}; \quad G_z - G'_z = \frac{2\pi}{a_z} a g_z, g_z \in \mathbb{R}$$

(3.22)
Now by comparing Eq. (3.21) and Eq. (3.22), it can be observed that $k_x = P_x g_x$, $k_y = P_y g_y$ and $k_z = P_z g_z$. For a chosen ($\overline{G} - \overline{G}'$) in Eq. (3.17), the integers $g_x$, $g_y$, $g_z$ are known from Eq. (3.22). Hence, plane wave expansion coefficients can be chosen as $\epsilon(\overline{G} - \overline{G}') = \epsilon(f_x, f_y, f_z) = \epsilon(P_x g_x, P_y g_y, P_z g_z)$. Due to periodicity of the Fourier transform, we need to make changes to the frequency bins as:

\begin{align*}
k_s &= P_s g_s; \forall 0 \leq P_s g_s \leq (N_s - 1) \\
k_s &= P_s g_s - N_s; \forall P_s g_s > (N_s - 1); \quad s = x, y, z; \\
k_s &= P_s g_s + N_s; \forall P_s g_s < 0
\end{align*}

(3.23)

In this way, the $\epsilon(\overline{G} - \overline{G}')$ matrix can be formed from the discrete Fourier transformation of the material mesh ($\epsilon(f_x, f_y, f_z)$). Now, inversion of the matrix $\epsilon(\overline{G} - \overline{G}')$ will give us $\kappa(\overline{G} - \overline{G}')$ as required to solve Eq. (3.17).

### 3.7.3 Band calculation of 3D periodic structures

The accuracy of the numerical PWE method has been tested here against well accepted band calculations for several structures with simple regular geometrical motifs. Figure 3.16 shows a closed-packed FCC structure of air spheres in silicon background. This well known FCC structure [29] has been used to demonstrate accuracy of numerical band calculation.

The analytical band calculation of this highly symmetric structure is shown in Fig. 3.17a. For the analytical PWE method closed form expression for Fourier transform of the sphere [51] has been used to solve Eq. (3.17) analytically. The corresponding numerical PWE band calculation of this structure is shown in Fig. 3.17b and can be compared directly with analytical band calculation shown in Fig. 3.17a. The $y$-axis of Fig. 3.17 shows the
Figure 3.16: (a) Closed-packed FCC structure of air spheres \((n_f = 1)\) in silicon background \((n_b = 3.45)\). (b) Brillouin zone (black) and irreducible Brillouin zone (red) of a FCC lattice [22].

Normalized frequency \((\omega/2\pi c)\) and x-axis shows scan path along the irreducible Brillouin zone shown in Fig. 3.16b. Both these band diagrams can further be compared with published results in [29]. For both analytical and numerical band calculation, 1331 plane waves were used to expand the structure shown in Fig. 3.16a. For numerical band calculation of Fig. 3.17b sampling frequency \((F_s)\) of \(F_s = 200\) samples/lattice constant has been used. From Fig. 3.17 it can be observed that the structure shown in Fig. 3.16a possesses a complete bandgap of \(\Delta\omega/\omega_o = 4.51\%\) between the seventh and eighth band as shown by the shaded region.

The accuracy of plane wave expansion critically depends on the number of plane waves used to solve the eigenvalue Eq. (3.17). Furthermore the accuracy of numerical band calculation also depends on sampling frequency used to create a discrete model of the actual structure for numerical plane wave expansion. The effect of number of plane waves and sampling frequency on convergence of band calculation has been demonstrated in the following sections. From the bandgap device design point of view, the bandgap centre frequency and bandgap width are the two most important parameters. Due to the impracticality of
tracking all minor variations of different bands with the change in number of plane waves or sampling frequency, in this study the percentage complete bandgap ($\Delta \omega / \omega_0 \%$) and bandgap centre frequency ($a \omega_0 / 2\pi c$) have been tracked to study the convergence of band calculation.

### 3.7.3.1 Dependence of band calculation on number of plane waves

The number of plane wave plays an important role in accurate band calculation of the plane wave expansion method as well as the computation time. Higher number of plane waves produces a more converged solution of the eigenvalue Eq. (3.17). Figure 3.18a shows variation of the percentage complete bandgap ($\Delta \omega / \omega_0 \%$) and Fig. 3.18b shows the corresponding variation of bandgap centre frequency ($a \omega_0 / 2\pi c$) with the number of plane waves for the structure shown in Fig. 3.16. Here, bandgap predictions of both analytical as well as numerical PWE method have been plotted as a function of number of plane waves. From Fig. 3.18 it can be observed that the bandgap predictions of the numerical PWE very closely match
Figure 3.18: Variation of (a) percentage complete bandgap ($\Delta \omega / \omega_o \%$) and (b) corresponding bandgap centre frequency ($a \omega_0 / 2 \pi c$) with number of plane waves of the structure shown in Fig. 3.16a computed using both numerical PWE as well as analytical PWE method.

bandgap predictions of the analytical PWE method.

From Fig. 3.18 it can be observed that with increase in the number of plane waves, the percentage bandgap and bandgap centre frequency converges. However, with the increase in the number of plane waves, the computation time increases exponentially as can be observed in Fig. 3.19 where band computation time of the FCC structure shown in Fig. 3.16a has been plotted as a function of number of plane wave and sampling frequency. Hence, we need to strike a balance between computation time and convergence accuracy.

We can observe from Fig. 3.18 that we require around 1000 plane waves to predict percentage bandgap with less than 4.2% error and bandgap centre frequency with less than 0.1% error compared to band calculation using 6859 plane waves, which is the highest number of plane wave used in this study beyond which there is no significant change in band calculation convergence accuracy.

A wide range of different 3D photonic crystal structures have been studied and it has been found that approximately 1000 plane waves is a good estimation for sufficient convergence...
Figure 3.19: Band computation time of the FCC structure shown in Fig. 3.16a has been plotted as a function of number of plane wave and sampling frequency.

accuracy of the band calculation.

3.7.3.2 Dependence of band calculation on sampling frequency

The accuracy of any numerical technique depends on discretization process of replicating the original structure into a discrete numerical model. To avoid aliasing effects, higher sampling frequency is always preferred for accurate representation of higher spatial frequency components of the real structure. However, higher sampling frequency requires higher computation memory. Hence, there needs to be a balance between structural accuracy and sampling frequency. Figure 3.20 shows the effect of sampling frequency on band calculation of the same closed packed FCC structure of air spheres in a silicon background as shown in Fig. 3.16a.

To highlight the importance of sampling frequency, bandgap predictions of numerical PWE have been compared with the analytical PWE method, which does not depend on sampling frequency. As predicted by the analytical PWE method, this structure possesses
a complete bandgap of 4.50% computed with 1331 plane waves. Corresponding numerical band calculation has been performed for a large range of sampling frequency of $F_s = 25$-200 samples/lattice constant using 1331 plane waves and the corresponding bandgap predictions have been compared with analytical PWE predictions. It can be observed in Fig. 3.20 that with the increase in sampling frequency, the numerical band calculation prediction of percentage bandgap and bandgap centre frequency converges to the corresponding analytical predictions. Hence, it can be concluded that to avoid aliasing related inaccuracies in the numerical bandgap calculation of a given structure, the sampling frequency should be above a threshold value. However, this threshold value depends on the spatial frequency contents of a given structure and hence will vary from structure to structure.

3.8 Summary

In this chapter, the theoretical foundation of the present research work has been laid out. The under-laying physics behind diffractive optics lithography has been discussed in terms of
Talbot self-imaging phenomenon. Lattice constants have been defined for the crystal lattice formed with a 3D periodic arrangement of Talbot self-images. The beam walk-off has been characterized to define a practical working depth of near-field. Effects of relative diffraction efficiency and polarization on near-field intensity distribution have been examined. The theory behind photonic band calculation has been discussed. Details of numerical band calculation have been elaborated with an example band calculation.
Chapter 4

Diffractive optics for fabrication of diamond-like structures

4.1 Introduction

A wide range of 3D photonic crystal structures have been proposed and fabricated over the past two decades [11]. 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 [24]. However, fabrication of diamond or diamond-like structures is challenging and tedious due to the double basis nature of their crystal geometry. In our diffractive optics lithography research, three DOE design have been proposed to fabricate diamond-like woodpile structure. In our initial work we have used 1D-DOE for two independent orthogonal laser exposures to fabricate diamond-like structure by interlacing two 2D periodic structures. To improve fabrication accuracy subsequently we present two single exposure methods based on phase-tunable and multi-level DOEs.
Figure 4.1: Diamond-like woodpile structure where \(a\) and \(c\) are lateral and axial periodicities respectively and \(S\) represents centre to centre distance between two orthogonally rotated log pile structures. \(R_x\) and \(R_z\) represent radii of elliptical shaped logs.

### 4.2 Diamond-like woodpile structure

A woodpile structure is characterized by stacking of two sets of orthogonally rotated logpiles as shown in Fig. 4.1. Here, \(a\) and \(c\) are lateral and axial periodicities, respectively, \(S\) represents the centre-to-centre distance between two orthogonally rotated log-pile structures, and \(R_x\), \(R_z\) represent radii of the elliptical shaped logs.

To fabricate a stable interconnected woodpile structure that does not collapse on development, it is advantageous to physically offset two set of orthogonally rotated log patterns in Fig. 4.1 with displacement, \(S\), while also having sufficient axial cross-section, \(R_z\), as defined in Fig. 4.1, that conservatively satisfy:

\[
R_z \geq \frac{c}{8}, \text{ and } \left(\frac{c}{2} - 2R_z\right) \leq S \leq 2R_z \tag{4.1}
\]

While \(R_z\) is defined by the laser exposure dose, polarization and the \(S\) offset requires precise
shift between the two set of log patterns. According to Eq. (4.1), \( R_z = \frac{c}{8} \) defines the lowest exposure threshold at which Eq. (4.1) demands an exact quarter period offset of \( S = \frac{c}{4} \), while any offset value is acceptable for \( R_z > \frac{c}{4} \).

4.3 Bandgap optimization of woodpile structure

From the ongoing development, it is evident that with suitable selection of optical materials and DOE design, a stable interconnected 3D woodpile structure can be fabricated following any of the three diffractive optics lithography methods explored here. While such woodpile structures can be classified as face centered cubic (FCC) or tetragonal (TTR) lattice symmetry [52], the TTR irreducible Brillouin zone is known to be a more appropriate symmetry [52] for woodpile structures. Hence, we base our band dispersion calculations on TTR symmetry. To predict the band positions, band dispersion curves were calculated using the numerical plane wave expansion (PWE) method as described in Section 3.7.2.

4.3.1 Complete bandgap

Calculations were carried out over a wide range of \( \frac{c}{a} \) ratios \( (1 < \frac{c}{a} < 3) \) and laser exposure levels (filling fractions of \( 10\% < f < 90\% \)) to identify the experimental exposure parameters that provide the widest bandgap for laser-formed templates inverted with silicon. The filling fraction could be controlled by varying any combination of laser intensity, polarization and exposure time as discussed in Section 3.6. Unlike the \( \frac{c}{a} \) ratio, the filling fraction has no closed form expression to produce a desired structure and required an iterative method of optimization. The \( \frac{c}{a} \) range was restricted by the \( \frac{\lambda_d}{\Lambda} \) ratio as defined in Eq. (4.2) by our choice of \( n_r = 1.6 \) for the refractive index of SU-8 photoresist, \( n_i = 1.9 \) for an incidence index.
matching medium, and \( n_d = 1.9 \) for a high index DOE substrate. The relative intensity of diffraction orders is controllable by the DOE etch depth as discussed in Section 3.5.1 and values of 30%, 30% and 30% were assumed for the \(-1^{st}\), \(0^{th}\) and \(1^{st}\) orders, respectively. The laser polarization was linear in both exposure orientations. The 3D intensity pattern was calculated for two equal intensity DOE exposures as described in Section 4.4.1 and then set to a threshold intensity that finally yielded an isointensity surface defining the 3D structure of the photoresist. This numerical calculation yielded an irregularly shaped motif, from which numerical band calculations [49] provided energy dispersion curves. A direct band calculation of the polymer structure with \( c/a = 1.2 \) and \( f \approx 25\% \) is shown in Fig. 4.2a. Values of \( S = c/4 \) and \( R_z = c/8 \) were selected to satisfy the interlacing condition (Eq. (4.1)) for a woodpile structure. This polymer structure provided an 8.1% bandgap along the Γ-Z direction—indicated by the hatching—but does not provide a complete photonic bandgap due to a low refractive index contrast of \( n_r - n_{air} = 0.6 \) for the photoresist template. However, if we double invert this structure using known procedures [16] to create a silicon log structure with an air background, a similar calculation yields the band dispersion curves of Fig. 4.2b where a complete bandgap of \( \Delta \omega / \omega_0 = 18.5\% \) is identified by the hatched area.

### 4.3.2 Optimized DOE parameters

The spectral width of the bandgap strongly depends on the \( c/a \) ratio, which, in turn, is easily controlled (Eq. 3.4) by the ratio of laser wavelength to DOE periodicity \( (\lambda_d/\Lambda) \). Figure 4.3 shows the dependence of complete bandgap width \( (\Delta \omega / \omega_0) \) for the double-inverted silicon structures with \( \lambda_d/\Lambda \) ratio for a constant filling fraction of \( f \approx 25\% \). The top axis shows the corresponding variation with \( c/a \) ratio. The maximum bandgap is noted at \( \lambda_d/\Lambda = \)
Figure 4.2: Band dispersion diagram (a) for 3D woodpile structure in photoresist for values of $n = 1.6$, $c/a = 1.2$, and $f \approx 25\%$ and (b) modified dispersion diagram with the same structure after double inversion to a silicon woodpile with $n = 3.45$, $c/a = 1.2$, and $f \approx 25\%$.

$0.98n_r \approx 1.57$ just before the cut off for total internal reflection at $\lambda_d/\Lambda = 1.6$. The energy dispersion curve in Fig. 4.2b is plotted for this maximum bandgap condition.

Flexibility of achieving a desired axial-to-transverse periodicity ratios, $c/a$, is crucial in fabricating photonic crystals because a complete photonic bandgap in such structures is available only in a narrow range of, $c/a$ ratio. DOEs provide wide latitude here for varying the $c/a$ ratio and thereby optimizing the bandgap properties. However, the maximum allowed value of the normalized wavelength ($\lambda_d/\Lambda$) is dictated by total internal reflection condition at various interfaces as given in Eq. (4.2). According to Eq. (3.4), $c/a$ depends principally on the DOE period ($\Lambda$), refractive index of the photoresist ($n_r$) and laser wavelength ($\lambda_d$) and is plotted in Fig. 4.4 as a function of the normalized wavelength, $\lambda_d/\Lambda$, for SU-8 photoresist ($n_r = 1.6$) following laser exposure arrangement of Fig. 3.2.

According to Fig. 4.4, the near-symmetric periodic structure can be achieved with a small period DOE such that $\Lambda \sim \lambda_d$. However, this condition yields high diffraction angles
Figure 4.3: Variation of the complete bandgap with $\lambda_d/\Lambda$ ratio for silicon inverted structures of silicon logs in air background ($f \approx 25\%$).

for the first order beams that will only propagate inside the DOE substrate for periods larger than the optical wavelength, $A > \lambda_d/n_d$ according to the generic laser exposure arrangement shown in Fig. 3.2. Total internal reflection at either of the DOE-incidence medium or the incidence medium-resist interfaces (Fig. 3.2) impose additional constraints of $A > \lambda_d/n_i$ and $A > \lambda_d/n_r$, respectively, that together limit the valid range of the $c/a$ data in Fig. 4.4 to a minimum value defined by the normalized wavelength

$$\frac{\lambda_d}{\Lambda} \leq \min\{n_d, n_i, n_r\}$$  \hspace{1cm} (4.2)

By substituting this limit into Eq. (3.4), one obtains the minimum $c/a$ value, for example, identified by the X-marks in Fig. 4.4, for different incidence media and assuming $n_d > n_i$. For air ($n_i = 1$), one can generate a minimum $c/a$ ratio of only 2.85. Alternatively, in the limit of using an index matching fluid with $n_i > n_r$, one obtains a symmetric periodic structure ($c/a \sim 1$) for $\lambda_d/\Lambda = n_r$. To access the full $c/a$ range of $1 < c/a \leq \infty$, the refractive index of DOE ($n_d$) and the incidence medium ($n_i$) must exceed the refractive index of the
Figure 4.4: Variation of $c/a$ ratio in SU-8 photoresist ($n_r = 1.6$) with normalized wavelength $\lambda_d/\Lambda$ for different refractive index values of the incidence medium ($n_i$).

Photoresist according to Eq. (4.3).

$$\{n_d, n_i\} \geq n_r; 1 < \frac{c}{a} \leq \infty$$  \hspace{1cm} (4.3)

Larger $n_i$ and $n_r$ values are attractive to reduce Fresnel losses, but exact $c/a = 1$ ratio is not achievable in this near-field diffractive optics method for any value of $n_d$, $n_i$ and $n_r$ because the condition $\lambda_d/\Lambda = n_r$ required to achieve $c/a = 1$ implies a diffraction angle of $\theta_1 = 90^\circ$ with no effective beam overlap region.

### 4.4 Diffractive optics for diamond-like structure

Due to the double basis, special DOE designs are required in order to create diamond-like near-field diffraction pattern. As mentioned in Section 3.3.1 a two-dimensional DOE is required for creating a 3D intensity distribution. However, a binary 2D DOE creates a 3D diffraction pattern of single basis structure arranged on body-centered-tetragonal (BCT) point Bravais lattice as shown in Fig. 3.2b. Hence, to circumvent this problem, in our
initial work we have used 1D-DOE for two independent orthogonal laser exposures to fabricate diamond-like structure by interlacing of two 2D structures. The required shift $S = c/4$ between two orthogonally rotated diffraction pattern is provided by precise physical displacement between DOE and sample between two laser exposures. To improve fabrication accuracy, we subsequently proposed two single laser exposure methods based on a phase-tunable DOE and a multi-level 2D-DOE. In the phase-tunable DOE method the shift $S$ is controlled by tuning the phase difference of one set of first order diffracted beams whereas in multi-level DOE method a fixed difference between the two phase levels was used to control the shift $S$.

4.4.1 One-dimensional DOE based double laser exposure method

Our group was first to extend DOEs to the fabrication of 3D photonic crystal templates, creating diamond-like woodpile structures in SU-8 photoresist by two sequential exposures of orthogonal one-dimensional DOEs (1D-DOE) with an Ar-ion laser [15, 43, 53]. In this section a general theoretical guideline for fabricating woodpile photonic crystal templates by the double-exposure 1D-DOE method is presented.

4.4.1.1 One-dimensional phasemask design

For demonstration purposes, two commercially available fiber Bragg grating writing fused silica ($n_d = 1.46$) phasemasks having period $\Lambda = 1.066 \mu$m and groove depth $d_t = 265 \text{ nm}$ have been used in fabricating woodpile structure using this double laser exposure method. The RCWA based diffraction efficiency calculation of the phasemask is shown in Fig. 4.5 for laser light of wavelength $\lambda_d = 488 \text{ nm}$ having polarization vector parallel to the grating grooves (TM polarized). According to the diffraction efficiency calculation the groove depth $d_t = 265 \text{ nm}$ have been used in fabricating woodpile structure using this double laser exposure method. The RCWA based diffraction efficiency calculation of the phasemask is shown in Fig. 4.5 for laser light of wavelength $\lambda_d = 488 \text{ nm}$ having polarization vector parallel to the grating grooves (TM polarized). According to the diffraction efficiency calculation the groove depth $d_t = 265$
Figure 4.5: Diffraction efficiency of the phasemask as a function of groove depth $d_t$ for period $\Lambda = 1.066 \, \mu m$, DOE refractive index $n_d = 1.46$ and background refractive index $n_b = 1.0$. The phasemask has been illuminated normally with laser light of wavelength $\lambda_d = 488 \, \text{nm}$ having polarization vector parallel to the grating grooves (TM polarized).

nm provides a $0^{th}$ order diffraction efficiency of $\eta_{00} = 55\%$, $1^{st}$ order diffraction efficiency of $\eta_{10} = \eta_{-10} = 20\%$ and $2^{nd}$ order diffraction efficiency of $\eta_{20} = \eta_{-20} = 0.7\%$ which closely follow experimental measurements of $\eta_{00} = 53\%$, $\eta_{10} = 19\%$ and $\eta_{20} = 1.5\%$, respectively, for $0^{th}$, $1^{st}$ and $2^{nd}$ order diffracted beams.

The present 1D phasemask of period $\Lambda = 1.066 \, \mu m$ produces a large $c/a = 7.29$ ratio for laser light of wavelength $\lambda_d = 488 \, \text{nm}$ that is not ideal for producing a complete photonic bandgap when inverted with a high refractive index material. DOE designs that can generate ideal lattice constants and filling fraction which will provide a complete bandgap are described in Section 4.3. Nevertheless, the present phasemask allowed us to demonstrate the feasibility of the proposed double laser exposure method of fabrication of woodpile structure in the optical domain.
Figure 4.6: Formation of multiple diffracted beams from a single laser beam by a 1D-DOE and arrangement for photoresist exposure.

4.4.1.2 Interlacing of two orthogonally rotated interference patterns

Figure 4.6 shows the separation of an incident laser beam into \( m = +1^{st}, 0^{th}, \) and \(-1^{st}\) diffraction orders after passing through a 1D-DOE of period, \( \Lambda = 1.066 \, \mu m \). In the overlap volume immediately below the DOE, the diffracted beams create a near-field 2D log-pile type interference pattern as shown in Fig. 4.7a. The 2D periodic interference pattern can be accurately captured with a thick \( (\gg c) \) negative photoresist placed in the beam overlap region of Fig. 4.6 and by applying a laser exposure that just exceeds the photo-polymerization threshold of the photoresist. Post exposure development then solidifies the polymerized volume and dissolves the under-exposed volume to replicate the interference pattern.

To create a 3D periodic structure, the first 1D-DOE exposure (Fig. 4.7a) is followed by a second exposure with an identical but orthogonally rotated 1D-DOE, creating the rotated...
Figure 4.7: Periodic near-field diffraction patterns created by (a) a single exposure with a 1D-DOE, (b) a single exposure with a similar 1D-DOE rotated by 90°, and (c) the resulting interlaced 3D woodpile structure due to combination of the two exposures in (a) and (b) with shift $S = c/4$ between two exposures.

2D log-pile intensity pattern show in Fig. 4.7b. The combination of these two sequential exposures then yields an intensity pattern approximately described by the interlaced 3D woodpile structure as shown in Fig. 4.7c. To form a double basis 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 by $S = c/4$ between two laser exposures.

Although, the figure cartoons in Fig. 4.7 depict uniform elliptical-like cross-sections with asymmetric radii, $R_x$ and $R_z$, the sum of two interference patterns are more complex than shown. A more precise representation of the intensity distribution can be easily generated by the methods in Section 3.5.2.2 with numerical computations that account for laser polarization together with the diffraction efficiencies and angles that depend on the groove depth and DOE period. The final structure of the photoresist is further governed by complex relations between laser exposure dose, photoresist exposure threshold, shrinkage and chemical diffusion. Such more accurate iso-intensity distributions will be presented and compared with observations of the fabricated structures in Chapter 6.
4.4.2 Phase tunable DOE for single exposure method

As discussed in the previous section, a diamond-like woodpile photonic crystal structure is to be formed with diffractive optics lithography by two sequential laser exposures of photore sist using two orthogonally rotated 1D binary phasemasks. However, imprecise alignment between two DOE exposures prevents this method from reproducibly interlace two 2D structures and a single exposure DOE method is therefore preferred for improved uniformity and reproducibility of the 3D structures. In this section, we present a phase-tunable DOE that has enabled formation of a 3D photonic crystal template with a single laser exposure. The phase-tunable DOE was constructed by orthogonal combination of two linear phase-masks. Controlled separation of the two optical elements provided a variable phase shift to manipulate the interlacing position of two orthogonally rotated periodic structures, and thereby facilitate fabrication of diamond-like woodpile structures having tetragonal (TTR) symmetry through to structures we predict to have body-centered-tetragonal (BCT) symmetry, and including variations in between. Finite difference time domain (FDTD) calculation of interference patterns and associated isointensity surfaces are corroborated by definitive demonstrations of TTR and BCT symmetry structures inside photoresist that smoothly transform from TTR to BCT symmetry by the DOE phase shift.

4.4.2.1 Phase tunable DOE

The proposed phase tunable DOE design for single-exposure 3D patterning centers on orthogonal alignment of two similar linear phasemasks, positioned back-to-back as shown Fig. 4.8. The DOE is illuminated at normal incidence by a laser beam of wavelength $\lambda_d$ as shown in Fig. 4.8. A pressure adjustable mount varies the separation, $d$, between the two phase-
Figure 4.8: Phasemask arrangement defining a two-dimensional DOE and providing adjustable separation, d, for phase shift control of near-field diffraction patterns.

masks to control the phase shift, $\Delta \phi$, between two 2D interference patterns generated in the z-x and z-y planes below the DOE. This gap or phase shift is pivotal in controlling the TTR-to-BCT symmetry by manipulating the near-field interference patterns formed inside the photoresist ($n_r$) positioned directly below the multi-level DOE. These patterns are modeled by diffraction theory [40, 54] given in Section 3.5.2.2.

4.4.2.2 Phase control principles

The top phasemask in Fig. 4.8 generates three strong diffracted beams of $h^1(0, 0)$ in zeroth order and $h^1(1, 0)$ and $h^1(-1, 0)$ in first orders, provided $\lambda_d / \Lambda < n_{gap}$ is satisfied. Here, $n_{gap}$ is the refractive index of the gap and the refractive index of both phasemasks is $n_d$. Due to different propagation paths, the $0^{th}$-order and $1^{st}$-order diffracted beams accumulate a phase difference prior to arrival at the second grating surface, given by:

$$\Delta \phi = \sum_i \overrightarrow{k}_{10}^i \cdot \overrightarrow{l}_{10}^i - \sum_i \overrightarrow{k}_{00}^i \cdot \overrightarrow{l}_{00}^i \quad (4.4)$$

where $\overrightarrow{k}_{10}^i$, $\overrightarrow{k}_{00}^i$ are wave vectors corresponding to $h^1(1, 0)$, $h^1(0, 0)$ diffracted beams respectively and $\overrightarrow{l}_{10}^i$, $\overrightarrow{l}_{00}^i$ are corresponding path vectors inside the $i$-th medium of the 2D-DOE.
For wave propagation through two phasemask substrates ($n_d$) of thickness $d_1$ and the gap ($n_{gap}$) between them of thickness $d$ and considering Snell’s law at each interface, the phase difference ($\Delta \phi$) becomes:

$$\Delta \phi = \frac{2\pi}{\lambda} \left[ \frac{n_{gap}d}{f(n_{gap})} + \frac{2n_d d_1}{f(n_d)} \right]$$

(4.5)

where

$$f(n_v) = \frac{\sqrt{1 - (\lambda_d / n_v \Lambda)^2}}{1 - \sqrt{1 - (\lambda_d / n_v \Lambda)^2}}, \text{ for } n_v = n_{gap}, n_d$$

These three beams are further diffracted by the second grating interface, creating the following five principle diffracted beams:

$$h^1(0,0) \Rightarrow \{ h^2(0,1), h^2(0,0), h^2(0,-1) \}$$

$$h^1(1,0)e^{j\Delta \phi} \Rightarrow \{ h^2(1,0) \} e^{j\Delta \phi}$$

(4.6)

$$h^1(-1,0)e^{j\Delta \phi} \Rightarrow \{ h^2(-1,0) \} e^{j\Delta \phi}$$

It is evident from Eq. (4.6) that 2D log-pile patterns are separately generated in each of the z-y and z-x planes by interference amongst the $h^2(0,1), h^2(0,-1)$ with $h^2(0,0)$ diffracted beams in the former and the $h^2(1,0), h^2(-1,0)e^{j\Delta \phi}$ with $h^2(0,0)$ diffracted beams in the latter. A 3D periodic structure then results from the interlacing of these two 2D log pile structures inside the photoresist. Here, a small variation of phasemask gap, $d$, in Eq. (4.5) is seen in Eq. (4.6) to introduce a controllable phase shift, $\Delta \phi$, between these two orthogonal log patterns. In this way, one can spatially control this interlacing offset to manipulate the symmetry of the 3D periodic structure formed inside the photoresist of Fig. 4.8. The phase shift then yields a spatial offset, $S$, of the x- and y-oriented logs in the axial direction, which can be folded by the periodicity of the lattice into the reduced range $0 \leq S \leq c/4$ and defined by:
Figure 4.9: The 3D structure representations of DOE near-field diffraction patterns generated by interlacing of two 2D log structures: (a) BCT symmetry structure for $S = 0$, and (b) diamond-like woodpile structure with TTR symmetry for $S = c/4$.

$$S = \frac{c}{2\pi} \Delta \phi \quad \text{where} \quad S(0) = S\left(m\frac{c}{2}\right), \forall m \in \mathbb{Z}$$  \hspace{1cm} (4.7)

This range encompasses all available crystal symmetries that span from BCT at $S = 0$ to TTR at $S = c/4$. Figure 4.9a depicts the interlacing of x- and y-oriented logs on the same horizontal planes for the condition of $S = 0$ (or $c/2$) and these inter-penetrated logs get arranged with a single basis on a body centered tetragonal (BCT) lattice. The other extreme case of $S = c/4$ separates these to orthogonally rotated structures axially and hence logs get arranged with a double basis on a tetragonal (TTR) lattice defining a diamond-like woodpile structure as shown in Fig. 4.9b.

The structural symmetry cycles periodically between TTR (for $m = 1, 2, 3\ldots$) and BCT ($m = 2, 4, 6\ldots$) lattices as the phasemask gap, $d$, increases according to:

$$d = \left[\frac{m}{4} \frac{\lambda}{n_{gap} f\left(n_{gap}\right)} - \frac{2n_{d}d_{1}}{n_{gap} f\left(n_{d}\right)}\right] f\left(n_{gap}\right)$$  \hspace{1cm} (4.8)
4.4.2.3 Finite difference time domain predictions of phase tunable near-field diffraction pattern

To fabricate a woodpile structure with a phase-tunable DOE which will demonstrate complete bandgap after inversion requires an optimized DOE design as given in Section 4.3. A high refractive index material between the two phasemasks of \( n_{gap} > n_r \) is also required [55]. However, for experimental demonstration two commercially fabricated phasemasks having the same period \( \Lambda = 1.066 \mu m \) as used in the double exposure method of Section 4.4.1 were used here as back-to-back connected masks with air gap \( (n_{gap} = 1) \) between them. To better predict the 3D structures generated by the DOE device in Fig. 4.8, finite difference time domain (FDTD) computation was used to generate time averaged intensity distributions, \( <I(x,y)> \), in the photoresist layer (SU-8, \( n_r = 1.6 \)) for various air gaps \( (n_{gap} = 1), d, \) between two phasemasks. Plane wave TE polarized light of \( \lambda_d = 514 \) nm was propagated through the phase-tunable DOE where TE polarization is defined as polarization vector perpendicular to the grating grooves. Figure 4.10 shows 2D intensity distributions \( (<I(x,y)> \) calculated for a fixed \( z = z_o \) plane that intercepts the center of x-oriented logs. The image sequence runs a full cycle of \( S \) offset values that progresses from a TTR structure defined by \( S = c/4 \) for the gap \( d = 0.9084 \mu m \) (Fig. 4.10a), to a BCT structure at \( S = c/2 \) (or 0) for the gap \( d = 1.816 \mu m \) (Fig. 4.10b), to a TTR structure at \( S = 3c/4 \) (or \( c/4 \)) for the gap \( d = 2.725 \mu m \) (Fig. 4.10c), and returning to a BCT structure at \( S = c \) (or 0) for the gap \( d = 3.634 \mu m \) (Fig. 4.10d). As predicted, the intersection points of orthogonally overlapping logs for \( S = 0 \) (Fig. 4.10b) and \( S = c \) (or 0) (Fig. 4.10d) are identical and manifest in near-circular intensity profiles that are arranged on a periodic square grid corresponding to the top surface of the BCT lattice as shown in Fig. 4.9a. Patterns for \( S = c/4 \) (Fig. 4.10a) and \( S = 3c/4 \)
Figure 4.10: Time averaged intensity profiles calculated by FDTD for a constant \( z = z_0 \) plane, for increasing phasemask air gap \( (n_{\text{gap}} = 1) \) of (a) \( d = 0.9084 \mu\text{m}, S = c/4 \), (b) \( d = 1.816 \mu\text{m}, S = c/2 \) (or 0), (c) \( d = 2.725 \mu\text{m}, S = 3c/4 \) (or \( c/4 \)), and (d) \( d = 3.634 \mu\text{m}, S = c \) (or 0). Here, \( a = \Lambda = 1.066 \mu\text{m} \).

(or \( c/4 \)) (Fig. 4.10c) are also identical as expected, representing the top view of logs in a diamond-like woodpile structure similar to that shown in Fig. 4.9b.

4.4.3 Multi-level 2D DOE for single exposure method

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 \( S = c/4 \) shift between two orthogonal interference patterns required for diamond-like structure. To improve fabrication reproducibility of diamond-like structure, a single-DOE device with appropriate fixed phase-shift is therefore highly desirable. John and co-workers proposed a phasemask design based on orthogonal placement of linear phasemasks on opposite surfaces of a single DOE substrate [56], but this requires tedious etching and deposition processes on opposite surfaces of a substrate as well as precise control of separation between two 1D gratings. We proposed a single-surface multi-level 2D 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 [56], or the accurate physical separation of two DOEs for phase control [35], a phase shift was built into the single-surface DOE design which further enables ease of etching of diffractive elements on a single side of a substrate.

4.4.3.1 Two-level vs. proposed three-level 2D DOE

A two-level 2-dimensional DOE is characterized by two phase levels (binary) and two lattice constants. Figure 4.11a shows a two-level square lattice 2D DOE having groove depth of \(d\) and equal periodicities of \(\Lambda_x = \Lambda_y = \Lambda\). The DOE has groove refractive index \(n_d\) which is immersed in background refractive index \(n_b\) to define two phase levels of optical thicknesses \(n_d d\) and \(n_b d\) as shown in Fig. 4.11a. One typical laser exposure arrangement showing index matching medium \((n_i)\) between the DOE substrate \((n_s)\) and the photoresist \((n_r)\) layer which is spun onto a substrate of refractive index \(n_s\) has been shown in Fig. 4.11b. However, as described in Chapter 3, the Talbot self-images of a two dimensional DOE having two phase levels repeats along the optical axis forming a 3D diffraction pattern of single basis structure arranged on a body-centered-tetragonal (BCT) point Bravais lattice. This lead to the conclusion that more complex phase profile is required in order to fabricate double basis structures.

To form a double basis diamond-like structure, we propose a three-level DOE. Figure 4.12a 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 \(\Lambda_x = \Lambda_y = \Lambda\) and asymmetrical depths \(d_1\) and \(d_2\) of the orthogonal grooves. The DOE-patterned film has refractive index
Figure 4.11: (a) A two-level 2D DOE having groove depth of \( d \) and equal periodicities of \( \Lambda_x = \Lambda_y = \Lambda \). (b) One typical 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 \( n_s \).

Figure 4.12: A three-level DOE (a) color-coded for each phase level as defined by orthogonal grooves of periodicities \( \Lambda_x \) and \( \Lambda_y \), 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 \( n_s \).

\( n_{d1} \) (blue) and \( n_{d2} \) (green) which is immersed in background refractive index \( n_b \) to define four different phase levels. For \( n_d = n_{d1} = n_{d2} \), 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. 4.12a.

4.4.3.2 Working principles of three-level DOE

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 DOE mentioned above 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 a more attractive double basis diamond-like structure. As noted in [35], an offset distance of \( S = c/4 = Z_T(n_r)/4 \) separates these two orthogonally rotated log-pattern type self-images axially inside the photoresist \((n_r)\) forming a double basis diamond-like structure. The \( S = c/4 \) offset between two orthogonally rotated logs inside photoresist \((n_r)\) can be mathematically proved to equal quarter period offset between the Talbot self-images associated with two diffractive structures of groove depths \( d_1 \) and \( d_2 \) and given as:

\[
|d_2 - d_1| = \frac{Z_T(n_b)}{4} = \frac{\lambda_d/n_b}{4[1 - \sqrt{(1 - (\lambda_d/n_r \Lambda)^2)}]} ; \forall S = \frac{c}{4} = \frac{Z_T(n_r)}{4} \tag{4.9}
\]

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

### 4.4.3.3 Three-level DOE design

As described in Section 4.3, in targeting to meet the relative crystal axis ratio \( c/a = 1.2 \) condition for a wide complete photonic bandgap requires a normalized wavelength \( \lambda_d/\Lambda \approx 0.98n_r = 1.57 \) (assumes the photoresist template is double inverted into silicon) [43]. To meet this condition for a high diffraction angle one must also avoid total internal reflection at the various interfaces by ensuring that \( n_d > 0.98n_r, n_b > 0.98n_r \) and \( n_i > 0.98n_r \). To achieve this \( c/a \) with our present combination of \( \lambda_d = 514 \text{ nm} \) (argon ion) laser and high resolution photoresist (MicroChem, SU-8, \( n_r = 1.6 \)) would require a small DOE period of \( \Lambda \)
= 327 nm which is beyond our present multi-level DOE fabrication capabilities of period \( \Lambda \sim 650 \) nm. A longer source wavelength of \( \lambda_d \approx 1020 \) nm was not a desirable alternative due to the poor response of photoresist at this wavelength and lower overall expected resolution. A compromise of a larger \( c/a \) ratio was necessary. Commercial DOEs are now available as a binary 2D phasemask with periods typically around 1 \( \mu \)m. Multi-level masks with high resolution features on the scale of \( \sim 250 \) 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 \( \mu \)m) photoresist (SU-8 2002, \( n_d = 1.6 \)) 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 \( \Lambda = 650 \) nm was selected as the minimum practical value for testing the proposed 3-level DOE design. However, according to Eq. (3.4), this combination predicts a large \( c/a \) ratio of 3.78 than the \( c/a = 1.2 \) 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 \( c/a = 1.2 \) ratio. Nevertheless, the proposed \( c/a = 3.78 \) ratio is a significant improvement over our previous demonstration of \( c/a = 6.91 \) which was based on much larger grating period of \( \Lambda = 1.066 \mu \)m [35,43,55]. 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 \( \Lambda = 650 \) nm period and \( \lambda_d = 514 \) nm laser wavelength, groove depths, \( d_2 \) and \( d_1 \), were optimized to balance and ideally distribute the intensities of the various DOE diffraction orders to produce an 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
Figure 4.13: Diffraction efficiency of a three-level DOE (Fig. 4.12a) as a function of groove depth $d_1$ with a fixed groove difference $(d_2 - d_1) = 331$ nm for diamond-like structure. Inset (i) shows the unit cell with $d_2$ and $d_1$ phase elements of refractive index, $n_d = 1.6$, in air background ($n_b = 1.0$) and substrate refractive index $n_s = 1.46$.

A fixed value of $(d_2 - d_1) = 331$ nm was obtained from Eq. (4.9) for the $S = c/4$ offset required for a diamond-like woodpile structure. To avoid high aspect ratio DOE grooves that might be difficult to laser-fabricate in the SU-8 photoresist ($n_d = 1.6$), an air ($n_b = 1.0$) background was selected for maximum index contrast. Figure 4.13 shows diffraction efficiencies calculated as a function of DOE groove depth $d_1$ by rigorous couple wave analysis (RCWA) based commercial algorithm (GSolver Ltd.). Circularly polarized plane wave light was used to avoid the strong polarization effects that otherwise imbalance (i.e. $\eta_{10} \neq \eta_{01}$) the x- and y-direction 1st order DOE diffraction efficiencies [55]. The color coded unit cell of the phase profile used in the diffraction efficiency estimation is shown in the inset-(i) of Fig. 4.13. The area of phase element $d_2$ occupies 50% of total area of the unit cell and $d_1$ and background ($n_b$) phase elements occupy 25% of total area each. For this combinations of laser wavelength ($\lambda_d = 514$ nm), DOE period ($\Lambda = 650$ nm) and substrate refractive index

84
(n_s = 1.46), there is no higher order diffracted beams (|m|, |n| ≥ 2) as well as due to very low diffraction efficiencies of < 1%, the 1st order cross beams (|m| = |n| = 1) has been ignored. To ensure uniform 3D intensity distribution and better local laser exposure dose control, according to Fig. 4.13 DOE groove depths \( d_1 = 1.13 \) µm, thus yielding \( d_2 = d_1 + 0.331 \) µm = 1.46 µm depth for the c/4 offset were chosen so that diffraction efficiencies of all 1st order beams are equal for a constant \( (d_2 - d_1) = 331 \) nm. The estimated diffraction efficiencies for this design are \( \eta_{00} = 55\% \) for 0th order and \( \eta_{10} = \eta_{-10} = \eta_{01} = \eta_{0-1} = 10\% \) for the first order beams.

### 4.4.3.4 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, finite difference time domain (FDTD) computation was used to generate time averaged intensity distributions, \(<I(x, y, z)>\), of the near-field diffraction pattern. For comparison purposes the near-field intensity distribution of a two-level 2D DOE shown in Fig. 4.11 was calculated as well.

#### A. Two-level DOE

The two-level DOE was custom designed and commercially fabricated on fused silica substrate \((n_d = 1.46)\) with a period of \( \Lambda_x = \Lambda_y = \Lambda = 570 \) nm, duty cycle = 50% and groove depth of \( d = 0.565 \) µm. The estimated diffraction efficiencies for this design are \( \eta_{00} = 41\% \) for 0th order and \( \eta_{10} = \eta_{-10} = \eta_{01} = \eta_{0-1} = 13\% \) for the 1st order beams for circularly polarized plane wave light of \( \lambda_d = 514 \) nm. A circularly polarized plane wave light of \( \lambda_d = 514 \) nm was first propagated through the two-level 2D DOE through the glass substrate.
Figure 4.14: Near-field isointensity distribution computed by FDTD showing a single basis BCT symmetry structure as expected from the two-level DOE of $\Lambda = 570$ nm, $d = 0.565 \mu m$, $n_d = 1.46$. Inset (b) and (c) shows 2D intensity distribution ($<I(x, y)>$) of two planes clearly shows the BCT symmetry of the single basis structure.

$(n_s =1.46)$, the index matching fluid ($n_i = 1.604$), the photoresist ($n_r =1.6$) as arranged in Fig. 4.11b. The calculated near-field intensity distribution having intensity contrast of, $C = (I_{max} - I_{min}) / (I_{max} + I_{min}) = 94\%$, was passed through a step-function threshold to closely mimic the photoresist response, yielding the 3D isointensity distribution as shown in Fig. 4.14a. As expected a 3D structure made with periodic arrangement of ellipsoid like motif on BCT point Bravais lattice is clearly evident with expected values of $a = 570$ nm, $c = 1.84 \mu m$. The 2D intensity distributions ($<I(x, y)>$) of inset (b) and (c) clearly shows the BCT symmetry of the single basis structure.

B. Three-level DOE

Finally, circularly polarized plane wave light of $\lambda_d = 514$ nm was propagated through the three-level DOE design described in Section 4.4.3.3 ($\Lambda = 650$ nm, $d_1 = 1.13 \mu m$, $d_2 = 1.46$
Figure 4.15: Near-field isointensity 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 $\Lambda = 650$ nm, $d_1 = 1.13 \mu$m, $d_2 = 1.46 \mu$m, $n_d = 1.6$ and $n_b = 1.0$. Inset (b) and (c) shows 2D intensity distribution ($\langle I(x, y) \rangle$) of two planes separated axially by $S = c/4 = 615$ nm distance which show orthogonally rotated log like intensity distributions as expected for a woodpile structure.

$\mu$m, $n_d = 1.6$, $n_b = 1.0$) through 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. 4.12b. The calculated near-field intensity distribution having intensity contrast of, $C = (I_{max} - I_{min}) / (I_{max} + I_{min}) = 96\%$, was passed through a step-function threshold to closely mimic the photoresist response, yielding the 3D isointensity distribution as shown in Fig. 4.15. The stacking of orthogonally rotated logs in woodpile structure is clearly evident with expected values of $a = 650$ nm, $c = 2.46 \mu$m, and axial shift between two orthogonally rotated logs $S = c/4 = 615$ nm forming double basis of a diamond-like structure. The 2D intensity distributions ($\langle I(x, y) \rangle$) of inset (b) and (c) clearly shows the orthogonal log structure offset by the $S = c/4 = 615$ nm quarter period.
4.5 Summary

In this chapter the woodpile structure has been introduced. The band diagram of an optimized woodpile structure is presented and corresponding variation of width of complete bandgap with normalized laser wavelength ($\lambda_d/\Lambda$) has been demonstrated. The theory behind three DOE techniques have been presented for fabrication of diamond-like structure. We started with 1D-DOE and then gradually moved to multi-level 2D-DOE for fabrication of diamond-like structure in a single laser exposure step. Finite difference time domain calculation of near-field diffraction patterns and associated isointensity surfaces corroborated definitive demonstration of a diamond-like woodpile structure formed inside photoresist.
Chapter 5

Experimental

5.1 Experimental

In this chapter, the CW argon ion laser and beam delivery system for diffractive optics lithography is discussed. In addition, the procedures for sample preparation and 3D periodic structure characterization are discussed.

5.1.1 Laser system

In the context of the present research work, any CW or quasi-CW laser could have been used to fabricate 3D structures as long as there is an optically transparent photoresist which is sensitive to the laser wavelength. Due to availability of a CW argon ion (Ar+) laser (Coherent, Innova Sabre MotoFred), this laser was selected in fabricating a wide range of 3D structures by the proposed diffractive optics methods described in Chapter 4. The argon ion laser has two strong wavelengths at $\lambda = 488 \text{ nm}$ and $514 \text{ nm}$ providing 10 W of power at each wavelength. The laser produces a linearly polarized light of beam diameter 5 mm (null-to-null). The laser is also attractive for high spatial and temporal coherence.
5.1.1.1 Beam delivery system

The beam delivery system of the argon ion laser is shown in Fig. 5.1. Turning mirrors ($M_n$) were used to divert the laser beam from laser head to sample exposure stage. The combination of half waveplate (HWP)-polarizer-quarter waveplate (QWP) was used to control the polarization state of the laser beam.

The spatial beam quality has been improved by spatial filtering of the beam. The spatial filter assembly (SF) consists of an objective lens of NA = 0.1 and gold plated pinhole of diameter = 10 $\mu$m. The filtered beam was collimated by a convex lens ($L_1$) and expanded with a beam expander (BE). The beam expander provides a beam expansion of 2-8 times. The expanded beam was flexibly apertured to diameter in the range of 5 mm-10 mm by an aperture ($A_b$). The laser exposure was controlled by an electronic shutter (ES). The sample was mounted on a six axis stage using vacuum suction of vacuum pumps (VP). The
photograph of the actual experimental setup has been shown in Fig. 5.2 with key components labeled.

5.1.1.2 Beam profile

For generating a uniform 3D near-field diffraction pattern, ideally a “top-hat” exposure laser beam profile is required. Unfortunately, the argon-ion laser used in this research, was extremely non-ideal with many hot spots on beam profile as can be seen in Fig. 5.3a and in corresponding single line intensity distribution in Fig. 5.3b. The laser beam profile was measured in front of the laser head before M₁ mirror as depicted in Fig. 5.1. The laser beam was improved with spatial filtering and subsequent beam expansion to mimic a top-hat beam profile. Figure 5.3c shows the 2D beam profile and (d) the corresponding single line intensity distribution after spatial filtering. The beam profile was measured after aperture A₇ with aperture A₇ set at 5 mm diameter. The beam was further expanded by 4 times with a beam expander (BE) and the expanded beam was apertured with the aperture A₉ of 10
5.1.2 Sample preparation

A negative photoresist of SU-8 from MicroChem was used for fabrication of 3D structures. Because SU-8 is optimized for i-line exposure (365 nm), photo-initiator (Spectra Group, H-Nu 470, 0.1% - 0.5% wt) and accompanied photo-coinitiator (Spectra Group, OPPI, 2.5% wt) was added to improve SU-8 response at 488 nm and 514 nm wavelengths. The absorption spectrums of H-Nu photoinitiators are shown in Fig. 5.4. The H-Nu 470 has peak absorption at 470 nm with broad absorption range from 350 nm to 530 nm which covers both our 488
nm and 514 nm laser wavelengths. Other two H-Nu photoinitiators, H-Nu 535 and H-Nu 635 have peak absorption at 535 nm and 635 nm respectively.

A uniform 15-30 µm thick resist layer was spun onto glass substrates. The sample was soft baked and exposed with argon ion laser light. Detailed sample preparation is given in Appendix-B.

5.1.3 Post exposure baking and development

Laser exposure of the photoresist was followed by two steps of post-exposure baking (3 min at 65°C and 5 min at 95°C) to complete the polymerization process. The baked sample was naturally cooled to 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. The
SU-8 photoresist shrinks after development which is an unfortunately common problem with thick SU-8 photoresist. A wide range of SU-8 shrinkage between 5%-15% has been reported in literature [35, 43, 57] which depends on photoresist preparation, post exposure baking and development process [57].

5.1.4 Characterization

Three-dimensional nanostructures are characterized in two steps. First they are characterized structurally to assess quality of the 3D structure. Subsequently, good quality 3D structures are probed optically for stopgap measurement.

5.1.4.1 Structural characterization

To ascertain periodicity along all three dimensions, the top as well as the cross-sectional views of the structure need to be evaluated. Due to sub-micron feature sizes, a scanning electron microscope was used. For cross-sectional view, the 3D structures were cleaved by scratching the substrate with diamond-cutter and breaking the sample along the scratch line using manual force. The manually cleaved sample was mounted vertically for cross-sectional SEM. In special circumstances for clean cleaving of 3D structures, focused ion beam (FIB) was used for in-situ milling and observation of the structure using a FIB/SEM combination in the Nanofabrication facility of University of Western Ontario.

A. SEM

The SEM (SEM, Hitachi S-5200) images were taken in Centre for Nanostructure Imaging facility of University of Toronto. For top view, the sample was mounted horizontally on a SEM stub using carbon paste. Polymer samples were manually cleaved and mounted
vertically for cross-sectional SEM observation. Due to low conductivity, the polymer SU-8 structures were carbon coated before SEM. For carbon coating a high vacuum carbon coater was used (Emitech High vacuum Carbon coater). A thin layer (300-400 Å) of carbon was deposited on the polymer sample following 60 sec - 90 sec evaporation time for a set evaporation current of 16-17 ampere. For better electron mobility, a conductive contact is made between deposited carbon layer and metal SEM stub using a tiny amount of carbon paste. During SEM a 1kV voltage and 20-25 μA emission current was used for imaging of the polymer structure.

B. FIB

Ideally all 3D structures should be milled with FIB for smooth high quality cross-sectional views. Manual cleaving creates irregularities and distortions of the cross-sectional SEM image of the structure. However, in this research, only silica inverted structures were milled with FIB at University of Western Ontario.

5.1.4.2 Optical characterization

A. Near-infrared transmission measurement

Samples were probed along the Γ-Z direction (normal incidence) with a fourier transform infrared (FTIR) spectrometer (Bruker, Tensor 27) in the 1.4-μm to 5-μm spectral range. The 10 mm diameter beam size of the FTIR, was apertured to 1 mm beam diameter for probing 3D samples. All spectral recordings were normalization against a reference spectrum recorded through an identical substrate coated with a fully developed solid resist coated to same thickness of the sample.
B. Telecom band transmission measurement

Transmission spectra were recorded in the 1.25\(\mu\)m to 1.65 \(\mu\)m spectral range on a fiber-to-fiber U-bench using a broadband light source (Agilent, 83437A) collimated to 500-\(\mu\)m diameter \((1/e^2\) intensity\), a rotatable sample mount, and an optical spectrum analyzer (Ando, AQ6317B). All spectral recordings were normalization against a reference spectrum recorded through an identical substrate coated with a fully developed solid resist coated to the same thickness of the sample.
Chapter 6

Fabrication using one-dimensional diffractive optics

6.1 Introduction

Our group was first to extend DOEs to the fabrication of 3D photonic crystal templates, creating diamond-like woodpile structures in SU-8 photoresist by two sequential exposures of orthogonal one-dimensional DOEs (1D-DOE) with an Ar-ion laser \([15, 43, 53]\). The present chapter builds on this sequential DOE-exposure method \([43, 58]\) by improving the fabrication precision of woodpile photonic crystal templates and, for the first time, spectroscopically characterizing the templates to verify their 3D structure against energy band models. Thick, large-area periodic nano-structures are confirmed to have woodpile structure closely matching the computed optical interference iso-intensity surfaces. However, imprecise alignment between two DOE exposures prevents this method from reproducibly interlace two 2D structures and a single exposure DOE method is therefore preferred for improved uniformity and reproducibility of the 3D structure. The phase-tunable DOE has enabled DOE formation of 3D photonic crystal templates with a single laser exposure. The controlled separation of the two optical elements provided a variable phase shift to manipulate the interlacing
position of two orthogonally rotated periodic structures, and thereby facilitate fabrication of diamond-like woodpile structures having tetragonal (TTR) symmetry through to structures we predict to have body-centered-tetragonal (BCT) symmetry, and including variations in between. Finite difference time domain (FDTD) calculation of interference patterns and associated iso-intensity surfaces are corroborated by definitive demonstrations of TTR and BCT symmetry structures inside photoresist that smoothly transform from TTR to BCT symmetry by the DOE phase shift.

The spectroscopic characterization of these templates reveals numerous low and high energy stopbands along preferential crystallographic directions that are consistent with calculated band dispersion curves for the low-index media. The results demonstrate good structural uniformity through a relatively large resist thickness and over large exposure area.

6.2 One-dimensional DOE for double laser exposure method

6.2.1 Laser exposure setup

In our initial work we have used a 1D-DOE which creates a 2D log-pile type near-field diffraction pattern. To create a 3D periodic structure, the first 1D-DOE exposure is followed by a second exposure with an identical but orthogonal 1D-DOE, creating the rotated 2D log-pile intensity pattern. Between two laser exposures a high precision motion control stage is used to move one DOE mask with respect to the sample surface ($n_r$) to interlace two 2D structures with quarter period shift ($S = c/4$) along the optical axis as shown in Fig. 6.1. The combination of two sequential exposures then yields an intensity pattern described by the interlaced diamond-like woodpile structure as discussed in Section 4.4.1 of Chapter 4. To facilitate translation between two 1D DOEs using a x-motion stage as well as axial shift
using a z-motion stage, an air gap \((n_i = 1.0)\) is maintained between DOE and sample surface.

### 6.2.2 Fabrication of 3D woodpile structures

Three-dimensional woodpile templates were patterned into photoresist by two sequential exposures of a cw argon ion laser at 488-nm wavelength through two orthogonal 1D-DOEs, each a linear phasemask with \(\Lambda = 1.066 \mu m\) period. Photo-initiator was added (0.1 wt \%) to improve SU-8 response at 488 nm. A uniform 15 \(\mu m\) thick resist layer was spun onto glass substrates following the recipe discussed in Appendix-A. Periodic structures of \(a = 1.066 \mu m\) and \(c = 7.29 \mu m\) were expected inside the negative photoresist according to Eq. (3.4). To avoid surface damage, an \(\sim 0.2 \text{ mm}\) air gap was maintained between the DOE and the photoresist during alignment and exposure. Two consecutive 1D-DOE exposures produced interlaced orthogonal log patterns with shift \(S = c/4\) to create the woodpile structure as predicted in Section 4.4.1. A 5-second exposure was applied through each 1D-DOE at 650
mW power over 3 mm diameter (full-width half maximum, FWHM) laser exposure area which was followed by two steps of post-exposure baking of the resist to complete the polymerization process after laser exposure. Fig. 6.2 shows the scanning electron beam microscope images of the top view (a) and cross-sectional view (b) of the photoresist after two orthogonal DOE exposures and development. A woodpile 3D photonic crystal structure is clearly evident with lateral periodicity of $a \approx 1.05 \mu m$ and axial periodicity of $c \approx 6.27 \mu m$.

Because the photoresist is bonded to the glass substrate, there is little lateral shrinkage ($\sim 1\%$) of the resist as the observed lateral period ($a \approx 1.05 \mu m$) closely matches the $\Lambda = 1.066 \mu m$ grating period as predicted by Eq. (3.4). On the other hand, the axial period ($c = 6.27 \mu m$) is 14% smaller than the expected $c = 7.29 \mu m$ value, which is attributed to resist shrinkage during development, an unfortunately common problem with thick SU-8 photoresist [43, 59]. The cross-sectional view in Fig. 6.2b shows uniform structure formation across the full 13 $\mu m$ thickness of the developed photoresist, supporting our assertion that the DOE method can produce thick photonic crystal templates in photosensitive materi-
als. A 3D periodic structure extended fully across the ∼2000μm diameter exposure area. Iso-intensity surface calculations were carried out as briefly described in Section 3.5.2.1 to match the observed SEM structure and are shown overlaid as inset (i) and (iii) in Fig. 6.2. Resist shrinkage was taken into account in the simulation by anisotropic scaling by a 14% axial shrinkage factor. The SEM observations are accurately replicated by the iso-intensity calculations over a large sample area. The SEM in Fig. 6.2b-(ii) provides values of $R_x = 0.23 \mu m$, $R_z = 1.45 \mu m \approx c/4.32$ and $S = 1.55 \mu m \approx c/4.05$. These values satisfy the interlacing conditions of Eq. (4.1) for formation of a stable, interconnected 3D structure. The SEM images provide an estimated filling fraction of $f \approx 69\%$, which closely corresponds with the $f \approx 64\%$ value used to optimize the iso-intensity profile matching in Fig. 6.2. The interlacing offset, $S$, was difficult to control to $c/4$ precision across the full surface area of the photoresist using our present alignment stages. However, a slight non-parallel alignment (< 10 mrad) was introduced between the two DOE surfaces to slowly varying the $S$ offset across the 3-mm diameter (FWHM) laser exposure area which created a wide range of non-perfect ($S \neq c/4$) log-pile structures. The fabricated 3D structure was found to be smooth over large sample area (∼2000 μm diameter) with minimum resolvable feature size of ≤200 nm.

The surface morphology is relatively smooth with roughness of ∼10 nm that suggest low optical scattering loss. The slight tilting of the structure (Fig. 6.2b) has been attributed to lateral shrinkage of the top layer relative to a bonded (non-shrinking) bottom layer. With the present DOEs, various filling fractions could be reproducibly created by varying the exposure time (3 to 15 seconds) and laser power.

101
6.3 Phase tunable DOE for single exposure method

To overcome the inherently imprecise DOE alignment that arises between two laser exposures, a single laser exposure fabrication of 3D photonic crystals is highly desirable. In the first proposed method, back-to-back mounting of two commercial linear phasemasks with crossed grating orientation defined a phase-tunable DOE that permitted the fabrication of the diamond-like structure. The schematic of the phase-tunable DOE arrangement is shown in Fig. 6.3a. By simply tuning the phase difference of one set of first order diffracted beams with the physical separation between the two diffractive elements, a continuum of other 3D periodic structures that are tunable from the double basis diamond-like structure to a single basis structure having body-centered-tetragonal symmetry (BCT) were fabricated as described in Chapter 4.

6.3.1 Laser exposure setup

To improve fabrication reproducibility of diamond-like structure, a single-DOE device with an appropriate fixed phase-shift was proposed as shown in Fig. 6.3. Photonic crystal templates were fabricated with the phase tunable DOE arrangement of Fig. 6.3, using two identical fused silica phasemasks having period \( \Lambda = 1.066 \ \mu m \). 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 (\( \pi/2 \) to 0 radian) of one set of first order diffracted beams with the physical separation between the two diffractive elements [35].

The 3D laser near-field interference pattern was captured in a uniform photoresist layer,
Figure 6.3: Laser exposure setup of back to back connected two 1D-DOE forming a phase tunable DOE.

by exposing the photoresist through the DOE with a linearly polarized cw argon ion laser operating at 514-nm wavelength. A longer laser wavelength of 514 nm was chosen compared to 488 nm used in above mentioned double exposure method in order to reduce axial period $c$ from 7.29 $\mu$m to 6.91 $\mu$m. Photo-initiator was added (0.2 wt %) to improve the SU-8 response at 514 nm. A single 20-sec exposure at 2.65-W power (incident on DOE) with a 3-mm beam diameter (full-width half maximum) was followed by two steps of post-exposure baking to complete the polymerization process.

6.3.2 Woodpile structure with TTR symmetry

Figure 6.4 shows scanning electron microscope (SEM) images of the top view (a) and cross-sectional view (b) of the resulting 3D patterned photoresist. A woodpile photonic crystal structure is clearly evident, where axially shifted ($S \approx c/4$) log-patterns are evident in both top (a) and cross-sectional (b) views. The lateral periodicity of $a \approx 1.06 \mu$m in Fig. 6.4a and axial periodicity of $c \approx 6.13 \mu$m in Fig. 6.4b closely match theoretical expectations of 1.066 $\mu$m and 6.91 $\mu$m, respectively, with larger difference in the z axis periodicity due to
Figure 6.4: Top (a) and cross-sectional (b) SEM images of diamond-like woodpile structure with TTR symmetry fabricated using phase-tunable DOE method together with insets (i) and (ii), respectively, of matching isointensity surfaces computed by FDTD for $d = 2.725 \mu m$ and corresponding to $S = c/4$.

an 11.3% shrinkage that is typical during development of SU-8 photoresist.

### 6.3.3 Structure with BCT symmetry

By adjusting the mount pressure to change the DOE gap distance (Eq. (4.8)), one also obtains an effective $S = 0$ offset that produces the predicted BCT symmetry as shown in the SEM images of Fig. 6.5. As expected, the intersection points of orthogonally overlapping logs manifest in cylindrical photoresist structures as shown in Fig. 6.5a that are arranged on a periodic square grid corresponding to the top surface of the BCT lattice in Fig. 4.9a. The cross-sectional view in Fig. 6.5b reveals an inter-penetrating square-grid of ellipsoidal structures as expected for this BCT symmetry structure with no axial shift between two orthogonally rotated logs like the woodpile structure in Fig. 6.4b.

The observed structures in Fig. 6.4 and 6.5 are directly comparable with isointensity surfaces generated by the above 3D FDTD method for values of $d = 2.725 \mu m$ and $d = 3.634 \mu m$, respectively. These correspond to respective offsets of $S = c/4$ for TTR symmetry and
Figure 6.5: Top (a) and cross-sectional (b) SEM images of structure with BCT symmetry fabricated using phase-tunable DOE method together with insets (i) and (ii), respectively, of matching isointensity surfaces computed by FDTD for $d = 3.634 \mu m$ and corresponding to $S = c$.

$S = 0$ for BCT symmetry and yield the isointensity surfaces overlaid as inset (i) and (ii) in the respective top and cross-sectional views in both Fig. 6.4 and 6.5. It can be observed that isointensity calculations very closely match the SEM observations of both structures.

6.3.4 Fabrication of diamond-like structure with circularly polarized light

In the previous section, we reported fabrication of diamond-like structures using linearly polarized light for the DOE parameters given above. Because of polarization dependence, the relative measured diffraction efficiencies ($\eta_{mn}$) of 1st order to 0th order beam $\eta_{01}/\eta_{00} = \eta_{0-1}/\eta_{00} \sim 3$ along the z-x plane and $\eta_{10}/\eta_{00} = \eta_{-10}/\eta_{00} \sim 4$ along the z-y plane for DOE groove depth $d_t = 265 \text{ nm}$ resulted in a non-symmetric 3D intensity distribution between z-x and z-y planes. Circular polarization eliminates this polarization dependence in this case by balancing diffraction efficiencies ratios to $\eta_{10}/\eta_{00} = \eta_{-10}/\eta_{00} = \eta_{01}/\eta_{00} = \eta_{0-1}/\eta_{00} \approx 3.5$ which consequently produces symmetric intensity distribution compared to linearly polarized
Figure 6.6: Top (a) and cross-sectional (b) SEM images of diamond-like woodpile structures having TTR symmetry together with insets (i) and (ii), respectively, of corresponding intensity distribution ($<I(x,y)>$) computed by FDTD for $d = 2.725$ $\mu$m air gap between two phasemasks corresponding to shift $S = c/4$.

light. The key to obtain symmetric intensity distribution is to ensure equal diffraction efficiency of all 1$^{st}$ order beams which is automatically guaranteed by circular polarization for this DOE arrangement of two identical phasemasks.

Scanning electron microscope images of the top view (a) and cross-sectional view (b) of the resulting 3D patterned photoresist is shown in Fig. 6.6 for shift $S = c/4$. A diamond-like woodpile photonic crystal structure is clearly evident, where axially shifted ($S \approx c/4$) log-patterns are manifested in both top (a) and cross-sectional (b) views. The lateral periodicity of $a \approx 1.06$ $\mu$m in Fig. 6.6a and axial periodicity of $c \approx 6.21$ $\mu$m in Fig. 6.6b closely matches theoretical predictions of $a = 1.066$ $\mu$m and $c = 6.91$ $\mu$m, respectively, with larger difference in the $z$ axis periodicity due to a 10.1 % shrinkage. The observed structure in Fig. 6.6 is directly comparable with the intensity distribution ($<I(x, y, z)>$) predicted by the 3D FDTD calculation for values of $d = 2.725$ $\mu$m corresponding to shift $S = c/4$, and overlaid as inset (i) and (ii) in the top and cross-sectional views in Fig. 6.6 which very closely match the SEM observations of the fabricated structure.
With circularly polarized light, the fabricated 3D structure was found to be more symmetric between z-x and z-y planes and more uniform over larger sample area (\(~2\-3 \text{ mm diameter}\) compared to the structures made by linearly polarized light as reported in the Section 6.3.2. Moreover, uniformity of all 1
\text{st} order diffracted beams for circularly polarized light offers better control of local laser exposure dose.

6.4 Optical characterization

Although the refractive index of the photoresist (\(n_r = 1.6\)) is too small to create a wide photonic bandgap, stopbands are predicted from numerical band calculation along several crystallographic directions for woodpile structure. However, no such stopbands are predicted for single basis BCT symmetry structure. In both 1D-DOE based double and single exposure methods, DOE period of \(\Lambda = 1.006 \, \mu\text{m}\) was used which resulted in similar lateral and axial periods of woodpile structures having similar optical characteristics. Here only optical characterizations of woodpile structure fabricated using the double laser exposure method is presented.

6.4.1 Near-infrared characterization

The woodpile structure shown in Fig. 6.2 was probed along the \(\Gamma\)-Z direction (\(c\) axis in Fig. 6.2b for TTR symmetry) with a Fourier transform infrared (FTIR) spectrometer in the 1.4-\(\mu\text{m}\) to 5-\(\mu\text{m}\) spectral range. All spectral recordings were normalization against a reference spectrum recorded through an identical substrate coated with a fully developed solid resist coated to similar 13-\(\mu\text{m}\) thickness. The normalized transmission spectrum of the structure is shown in Fig. 6.7b. A strong absorption trough from 2.6 to 3.6 \(\mu\text{m}\) has been attributed
to intrinsic material absorption by the SU-8 film. Outside this band, a moderately strong stopband is noted at 4.45-\textmu m wavelength that we attribute to a $\Gamma$-Z direction stopband, together with several higher-order bands near 2 to 3 \textmu m. Diffraction losses due to the $a = 1.05$ \textmu m periodic planar structure are only possible for $\lambda < 1.45$ \textmu m. A narrow $\sim 45$-nm (FWHM) bandwidth indicates that all 9 layers seen in Fig. 6.2b are acting coherently. Hence, the DOE method of laser interference appears robust in replicating identical multi-layer periodic structures deeply throughout the resist. The band dispersion relation for this structure was calculated from the isointensity surface of Fig. 6.2 and is shown in Fig. 6.7a. This isointensity surface had been computed iteratively to match the SEM contours, the periodicity, and the ratio $c/a = 6.27/1.05 = 5.97$ observed in the fabricated structure. The computed filling fraction of $f = 64\%$ corresponds well with the approximate $f \approx 69\%$ value estimated from the SEM cross-sections. The observed stop band at 4.45 \textmu m closely matches the predicted stopband at 4.62 \textmu m ($a/\lambda = 0.2273$) in the $\Gamma$-Z direction of the energy dispersion curve as identified by the two horizontal lines crossing both figures. The predicted bandwidth of $\sim 58$ nm slightly exceeds the observed $\sim 45$ nm (FWHM) bandwidth.

These mismatches can be readily attributed to uncertainties in estimating the structural shrinkage, the filling fraction, the motif, and the refractive index of SU-8 ($n_r = 1.6$). The spectral response of the stopband was nearly invariant over relatively large sample area ($\sim 2000$ \textmu m diameter) confirming the good structural uniformity of the photonic crystal over the large exposure area. Figure 6.7a further reveals several narrow higher order bandgaps are also predicted in the band calculation, which however we could not be definitively assigned to the spectroscopic observations in Fig. 6.7b at the present time.
Figure 6.7: Band calculation (a) for double exposure formed woodpile template \((f = 64\%, c/a = 5.97, n_r = 1.6)\) shown in Fig. 6.2 and (b) infrared spectral recording along \(\Gamma\)-\(Z\) direction. (c) The Brillouin zone of the tetragonal lattice displaying scan path used in band calculation of (a) [22].

### 6.4.2 Telecom-band characterization

We further performed spectral characterization of stop bands at multiple angles of incidence from normal incidence (\(\Gamma\)-\(Z\)) up to \(\sim 70\) degrees from the surface normal in the azimuthal plane. A lower wavelength range of 1.2 - 1.6 \(\mu\)m was used to probe higher order bands. Transmission spectra were recorded on a fiber-to-fiber U-bench using a broadband light source collimated to 500-\(\mu\)m diameter (1/\(e^2\) intensity) as described in Section 5.1.4.2, a rotating mount for the sample holder, and an optical spectrum analyzer. A reference transmission spectrum was recorded for a solid photoresist-coated (\(\sim 13\)-\(\mu\)m thick) glass substrate for various angles between \(\pm 70\) degree and used to normalize the transmission spectra of the
woodpile samples. Aside from differences in Fresnel losses, no angular dependence effects were observed in the reference sample spectra. The normalized transmission spectra of the woodpile structure are plotted in Fig. 6.8 for various incident angles between 0 Deg and 24 Deg. High transmission with relatively flat spectral response was noted for all angles from 0 Deg to 16 Deg. Three strong attenuation troughs started to appear around 16 Deg angle of incidence at $\sim 1280$ nm, 1397 nm and 1541 nm with spectral spacing of 117 nm and 144 nm, respectively. The spectral attenuation increases monotonically with angle from the approximate -1-dB baseline at 16 Deg to a peak value of approximately -22 dB at $\sim 21$ Deg. With further increase in angle of incidence, the attenuation diminishes and a flat high transmission spectrum is found again at $\sim 25$ Deg, which continues to remain high up to angle 70 Deg. As expected due to the crystal symmetry, the spectra follow similar angular dependence at negative angles of incidence as well. The spectral resonances are not due to Fabry-Perot resonances which would generate a much smaller free-spectral range for the 13-$\mu$m thick photoresist on 1-mm thick glass substrates.

It is interesting to observe that these stopgaps are present only for a narrow angular range. Given the $a \approx 1.05$-$\mu$m lattice constant and $\lambda = 1.2 - 1.6$ $\mu$m probing range, the range of $a/\lambda \approx 0.84 - 0.65$ corresponds to higher order bands. However, small uncertainties in the physical structure prevent sufficiently precise energy band calculations to permit definitive band assignments to these higher energy stop bands which remain open for such narrow range of angle. Nevertheless, the narrow angular resonances in Fig. 6.8 confirm the formation of a highly uniform 3D woodpile structure throughout the thick resist (13 $\mu$m) and over large area (2 mm diameter), which would otherwise be washed out by minor lattice distortions for such high-order bands. Such narrow angle spectral sensitivity can be exploited for various
Figure 6.8: Telecom-band transmission spectra through a woodpile template (Fig. 6.2) for various angles of incidence (degree) from the sample normal.

6.5 Discussion

Two 1D-DOE based double and single laser exposure method of 3D fabrication techniques have been demonstrated. Lin et. al. was first to use double laser exposure method to fabricate woodpile-type photonic crystal templates in photoresist [15]. However, we demonstrated improved fabrication precision and provide the first spectral characterization of woodpile photonic crystal templates formed by double laser exposure method. While double exposure method is relatively simple but suffers from alignment uncertainty between two laser exposures. The proposed phase-tunable DOE permitted the first single exposure near-field lithography based fabrication of the diamond-like structure. The phase-tunable single exposure method is more robust and versatile in generating a range of 3D structures, with symmetries from TTR through to BCT, that offer flexible tailoring of bandgap strength,
width, and spectral dispersion. A relatively long period DOEs ($\Lambda = 1.066 \, \mu m$) provided 3D templates in SU-8 photoresist that confirm formation of thick, large area periodic nanostructures with closely matched to optical interference iso-intensity predictions.

The present combination of DOE period ($\Lambda = 1.066 \, \mu m$), laser wavelength ($\lambda_d = 514$ nm) and photoresist ($n_r = 1.6$) produced a large $c/a \approx 6.48$ ratio that is not ideal for producing a complete photonic bandgap when inverted with a high refractive index materials. DOE designs that can generate ideal lattice constants and filling fraction for woodpile structure which will provide a complete bandgap are described in Section 4.3. Nevertheless, the spectroscopic characterization of the templates revealed numerous low and high energy stopbands along preferential crystallographic directions that were consistent with calculated band dispersion curves for the low-index media. The SEM and spectral observations show good structural uniformity through a relatively large resist thickness and over large exposure area that promise 3D photonic crystal devices with high optical quality.
Chapter 7

Fabrication using two-dimensional diffractive optics

7.1 Introduction

As introduced in Chapter 6, a woodpile structure was first formed with diffractive optic near-field lithography by two sequential laser exposures of photoresist using orthogonally rotated 1D binary phasemasks. To overcome the inherently imprecise DOE alignment that arises between two laser exposures, a single laser exposure fabrication of 3D photonic crystals was devised by back-to-back mounting of two linear phasemasks with crossed grating orientation. Although, the phase tunable near-field DOE method was versatile, it required accurate physical separation of the two orthogonally rotated gratings in order to provide a precise $c/4$ shift between two orthogonal interference patterns required for diamond-like woodpile structure. To improve fabrication reproducibility of diamond-like structure, a single 2D 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 [56], this design requires tedious etching and deposition processes on opposite surfaces of a substrate as well as precise control of
separation between two the 1D gratings.

In this chapter, we present a single-surface multi-level 2D 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 [56], or the accurate physical separation of two DOEs for phase control [35], a phase shift was built into the single-surface DOE design which further also enabled 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 \( (a = b = 650 \text{ nm} \text{ and } c = 2.46 \mu\text{m}) \) over our prior demonstrations \( (a = b = 1.06 \mu\text{m} \text{ and } c = 6.91 \mu\text{m}) \) as described in Chapter 6. The DOE was then applied to form diamond-like structures were fabricated in photoresist having \( \Gamma-Z \) (normal incidence) stopbands now shifted into the 1.25-1.65 \( \mu\text{m} \) telecom band from previous observations in the 3 to 5 \( \mu\text{m} \) spectral range.

### 7.2 Fabrication of two-dimensional diffractive optics

To demonstrate the effect of 2D DOE phase levels a two-level DOE was first custom designed and commercially fabricated using standard semiconductor lithography, and applied to fabricate a single basis BCT symmetry structure. The proposed three-level DOE was fabricated by two photon polymerization with a femtosecond laser and the three-level photoresist mask was used to fabricate a woodpile structure.
7.2.1 Two-level DOE

The two-level DOE was custom designed and commercially (Ibsen Photonics Ltd.) fabricated to create a high contrast near-field intensity distribution with much smaller periodicity of \( \Lambda_x = \Lambda_y = 570 \text{ nm} \). The 2D square lattice pattern was holographically created by the company using orthogonal two beam interference patterns and the photoresist pattern was subsequently transferred to fused silica substrate using reactive ion etching. Figure 7.1 shows an atomic force microscope image of the two-level DOE having 50% duty cycle and lateral feature size of \( \sim 285 \pm 10 \text{ nm} \). The measured diffraction efficiencies for the 0\(^{th}\) and 1\(^{st}\) order beams were \( \eta_{00} \approx 42\% \) and \( \eta_{01} \approx \eta_{0} \approx \eta_{-1} \approx 11\% \), respectively, for circularly polarized light which closely follows theoretical predictions of diffraction efficiencies of \( \eta_{00} \approx 40.5\% \) and \( \eta_{01} \approx \eta_{0} \approx \eta_{-1} \approx 12.8\% \) for an etched DOE groove depth of \( d_t \approx 0.595 \mu\text{m} \). The mask was found to be highly uniform over the entire 10 mm x 10 mm patterned area.

7.2.2 Three-level DOE fabrication by two photon polymerization

Unlike a two-level DOE, a custom designed three-level mask with high resolution features on the scale of \( \sim 250 \text{ nm} \) as per Section 4.4.3.3 was very challenging to fabricate and must be custom fabricated. The three-level DOE was fabricated in our group by Ladan Abolghasemi by two photon polymerization on thin (~2 \( \mu\text{m} \)) photoresist film (MicroChem, SU-8 2002) by femtosecond laser (IMRA, \( \mu\text{Jewel-D400-VR} \)) direct writing (\( \lambda = 522 \text{ nm} \), power = 100 \( \mu\text{W} \), 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 \( \Lambda_x = \Lambda_y \approx 650 \text{ nm} \) 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.
Figure 7.1: Atomic force microscope image of the two-level DOE of period $\Lambda_x = \Lambda_y = 570$ nm and etch depth $d_t = 595$ nm. Inset (i) show single-line height profile that define groove depths $d_t$ (Length of scale bars as indicated).

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 7.2 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 was found to be uniform over most of the 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 $d_1 \approx 1.05 \mu m$ and $d_2 \approx 1.37 \mu m$, respectively, along x and y directions. The inset (i) and (ii) in Fig. 7.2 show the $d_2$ and $d_1$ surface profiles along a-c and c-d phase segments, respectively, of an unit cell shown in inset (iii).

The difference in DOE groove depths $(d_2 - d_1) \approx 320$ nm closely satisfies Eq. (4.9) for a shift $S \approx c/3.86$ reduced to first phase shift zone of $0 \leq S \leq c/4$. Because of higher net laser exposure in the DOE line crossing points, an approximate $\pm 20$ nm height modulation results along the a-b groove direction as seen in the unit cell shown in Fig. 7.2-(iii). This
deviates from the uniform phase profile expected as shown in the A-B section of the unit cell of Fig. 7.2-(iv), leading to an unbalance of the diffraction orders. The measured diffraction efficiencies for the 0th and 1st order beams were $\eta_{00} \approx 48\%$, $\eta_{01} \approx \eta_{0-1} \approx 15\%$ and $\eta_{10} \approx \eta_{-10} \approx 8\%$, respectively, for circularly polarized light which closely follows theoretical predictions of diffraction efficiencies of $\eta_{00} \approx 56.7\%$ and $\eta_{01} \approx \eta_{0-1} \approx 13.7\%$ and $\eta_{10} \approx \eta_{-10} \approx 5.29\%$ for the inferred DOE groove depths of $d_1 \approx 1.05 \mu m$ and $d_2 \approx 1.37 \mu m$ determined by AFM scan. This deviation from the targeted diffraction efficiencies of $\eta_{00} = 55\%$ and $\eta_{10} = \eta_{-10} = \eta_{01} = \eta_{0-1} = 10\%$ 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 $d_2 = 1.46 \mu m$. This imbalance in diffraction order efficiency as well as non-ideal phase profile modified the 3D near-field diffraction pattern. However, the strong step-function like photoresist response mitigated these differences and hence the captured near-field pattern inside the photoresist closely resembles the original predictions of the ideal DOE diffraction pattern.

7.3 Single exposure fabrication of 3D photonic crystals

Figure 7.3 shows the laser exposure arrangement of (a) the two-level DOE shown in Fig. 7.1 and (b) the proposed three-level DOE shown in Fig. 7.2. Also shown the index matching medium ($n_i$) between the DOE substrate ($n_s$) and photoresist ($n_r$) layer which was spun onto a substrate of refractive index $n_s$. It is evident from the discussion in Section 4.3 that high index materials ($n > n_r$) are required to produce a highly symmetric ($c/a \sim 1$) photonic crystal template. For this reason, an index matching medium ($n_i$) is proposed between the DOE and photoresist in the laser exposure setup shown in Fig. 7.3. This allows propagation
Figure 7.2: Atomic force microscope image of the three-level DOE represented by the three different colors (heights). Enlarged section identifies a unit cell abcd (iii) and the ideal height profile ABCD (iv) used in the FDTD simulation. Inset (i) and (ii) show single-line height profiles in orthogonal scan directions that define groove depths $d_2$ and $d_1$ (Length of scale bars as indicated).

of diffracted beams with larger diffraction angle which otherwise do not propagate in the air gap between DOE and photoresist layer. This arrangement also further eliminates physical contact and damage to the DOE by the photoresist.

7.3.1 Single basis BCT symmetry structure using two level DOE

Single basis BCT symmetry structures were fabricated with the two-level 2D DOE arrangement of Fig. 7.3a. The 3D near-field diffraction pattern was captured in a uniform photoresist layer, by exposing the photoresist through the DOE with a cw argon ion laser operating at 514-nm wavelength. Photo-initiator was added (0.5 wt %) to improve the SU-8 response at 514 nm. A single 12-sec exposure at 1.25-W power (incident on DOE) with a 10-mm beam diameter (null-to-null) was followed by two steps of post-exposure baking to complete the polymerization process. Figure 7.4 shows scanning electron microscope (SEM) images of the top view (a) and cross-sectional view (b) of the resulting developed 3D patterned photoresist.
Figure 7.3: Laser exposure arrangement of a (a) two-level DOE and (b) the proposed three-level DOE 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 $n_s$.

A single basis BCT symmetry structure is clearly visible in Fig. 7.4. The lateral periodicity of $a \approx 570$ nm in Fig. 7.4(iii) and axial periodicity of $c \approx 1.54$ µm in Fig. 7.4(iv) closely match theoretical expectations of 570 nm and 1.84 µm, respectively, with larger difference in the z axis periodicity due to an 16.3 % shrinkage during development of SU-8.

Due to weak connectivity between ellipsoidal motifs, the formation of a stable single basis BCT symmetry structure is difficult. Precise laser exposure dose is required to fabricate a stable bi-continuous structure that also remains porous. In Fig. 7.4b, the 3D structure is seen to form with high uniformity through the full $\sim 25$ µm thickness of the photoresist, forming 22 distinct layers. A highly connected stable BCT symmetry structure is clearly visible in Fig. 7.4. The observed structure is directly comparable with isointensity surface computed by the 3D FDTD. For FDTD calculation, measured DOE parameters given in Section 7.2.1 were used. The resulting isointensity surfaces overlaid as inset (i) and (ii) in the respective top and cross-sectional views in Fig. 7.4 are seen to very closely match the SEM observations of the laser fabricated structure.
7.3.2 Double basis diamond-like structure using three-level DOE

The woodpile three-dimensional photonic crystals were fabricated in photoresist by a single exposure of a cw argon ion laser at 514-nm wavelength through the three-level DOE shown in Fig. 7.2 and using the laser exposure arrangement of Fig. 4.12b [36,60]. Photo-initiator (H-NU 470, 0.2% wt of SU-8) was added to improve SU-8 absorption at 514 nm. A 7 second exposure of photoresist ($n_r = 1.6$) using a collimated 6-mm diameter (null-to-null) beam of 3.15 W power was made in the arrangement of Fig. 4.12b through the index matching fluid of refractive index $n_i = 1.604$. This was followed by two steps of post-exposure baking to complete the polymerization process. Figure 7.5 shows scanning electron microscope images of the top view (a) and manually cleaved cross-sectional view (b) revealing 40 layers.
of the photoresist structure after exposure and development. A diamond-like woodpile 3D photonic crystal structure is clearly evident with lateral periodicity of $a \approx 650 \pm 30$ nm and axial periodicity of $c \approx 2.32 \pm 75$ $\mu$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 mean 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 the theoretical design ratio of $c/a = 3.78$. For a given set of optimized parameters, usually 4-5 samples were made. These structures found to be very similar. In some cases slight variation in filling fraction was observed which possibly due to a combination of causes like sample to sample minor variation of photo-initiator amount, minor variation of laser exposure dose between exposures. We also observed small variation in lattice constants. For the woodpile structure shown in Fig. 7.5, we measured 30 nm (std. variation) of lateral period variation and 75 nm (std. variation) of axial period variation.

In Fig. 7.5b, the 3D structure is seen to form with high uniformity through the full
∼25 thickness of the photoresist, forming 40 distinct layers. Most of the irregularities and distortions of the cross-sectional SEM image (Fig. 7.5b) of the structure came from the damage during manual cleaving of the 3D soft polymer structure. By controlling laser exposure dose, structures with a relatively wide range of filling fraction or porosity have been fabricated. Here, we intentionally chose the structure shown in Fig. 7.5 having a high filling fraction of ∼78% for its optical response in the telecom band as discussed in Section 7.4. A clear vertical offset of $S \approx 0.605 \mu m$ is noted between the orthogonally rotated logs in Fig. 7.5b-(iv) that closely matches the required ideal $c/4 = 2.46/4 = 0.615 \mu m$ shift, thus confirming a double basis of a diamond-like structure. This corresponds well with the shift $S \approx c/3.86$ value inferred from Eq. (4.9) considering the periodic relation $0 \leq S \leq c/4$ for the DOE groove depth difference of $(d_2 - d_1) \approx 320 \text{ nm}$. The observed structure in Fig. 7.5 is directly comparable with iso-intensity surfaces computed by the 3D FDTD method, which was used to generate Fig. 4.15. For this calculation, the DOE unit cell was approximated with rectangular phase elements as shown by inset (iv) in Fig. 7.2, but using the measured AFM values of $d_1 \approx 1.05 \mu m$ and $d_2 \approx 1.37 \mu m$ inferred above. The resulting iso-intensity surfaces overlaid as inset (i) and (iii) in the respective top and cross-sectional views in Fig. 7.5 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 iso-intensity surface of inset (iii). This close correspondence between FDTD predictions and fabricated structures 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.
7.4 Optical characterization

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 woodpile structure shown in Fig. 7.5 along several crystallographic directions. However, no such stopband was predicted for single basis BCT symmetry structure shown in Fig. 7.4.

7.4.1 Telecom band transmission measurement

The sample shown in Fig. 7.5 was optically probed along the $\Gamma$-Z direction ($c$ axis in Fig. 7.5b) with a broad band source in the 1.25 $\mu$m to 1.65 $\mu$m spectral range. The normalized transmission spectrum is shown in Fig. 7.6b. 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$m thickness. At 1.306-$\mu$m wavelength, a strong -30dB attenuation stopband with narrow response of $\sim$20 nm (FWHM) is observed.

The strong and narrow stopband ($\sim$20 nm) indicates that all 40 layers in Fig. 7.5b are collectively acting as coherent planes indicating formation of a highly uniform 3D structure throughout the thick photoresist (30 $\mu$m) and over large area (2 mm diameter). This narrow high-order stopband would otherwise be washed out by minor lattice distortions. 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 normal incident ($\Gamma$-Z) stopband strength ($T$) and stopband location ($\lambda_0$) of the present polymer woodpile structure has been compared with other prominent groups in Table 7.1. Noda and co-workers used semiconductor lithography (SL) to fabricate woodpile structure in GaAs ($n = 3.4$) fol-
Figure 7.6: Band diagram (a) of the structure shown in Fig. 7.5 revealing a Γ-Z direction (normal incidence) (c-axis) stopband between the 5th and 6th band and corresponding normalized transmission spectrum (b) measured as normal angle of incidence through the structure in Fig. 7.5b showing a strong (-30 dB) stopband at 1.306 µm.

Following a layer-by-layer approach and observed a Γ-Z stopgap of -40dB at λ₀ = 1.3 µm [8]. Such strong stopband was observed due to high refractive index contrast (Δn = 2.4) of the woodpile structure fabricated in GaAs. However, as expected comparatively weak stopband was observed for polymer woodpile structure fabricated using direct laser writing (DLW) by other three groups listed in the Table 7.1 [9, 10, 61]. The strong stopband (-30dB) observed in the present work is attributed to the large number of layers (10 unit cells along the optical axis) of the fabricated woodpile structure which strongly compensate for the low refractive index contrast of the polymer-air structure.

### 7.4.2 Numerical band calculation

The band dispersion relation was numerically computed using the isointensity surface of the fabricated structure shown in Fig. 7.5-(i)-(iii) using the numerical plane wave expansion method described in Section 3.7.2. This isointensity surface had been computed iteratively
Table 7.1: Comparison of the normal incident ($\Gamma$-Z) stopband strength ($T$) and stopband location ($\lambda_0$) of the present polymer woodpile structure with woodpile structure fabricated by other prominent groups.

<table>
<thead>
<tr>
<th>Group</th>
<th>Method</th>
<th>$a$ ($\mu$m)</th>
<th>$c$ ($\mu$m)</th>
<th>$c/a$</th>
<th>$\Delta n$</th>
<th>Layers</th>
<th>$\lambda_0$ ($\mu$m)</th>
<th>$T$ (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noda and co-workers [8]</td>
<td>SL</td>
<td>0.7</td>
<td>0.84</td>
<td>1.2</td>
<td>2.4</td>
<td>8</td>
<td>1.3</td>
<td>-40</td>
</tr>
<tr>
<td>Present work [36]</td>
<td>DOE</td>
<td>0.65</td>
<td>2.32</td>
<td>3.57</td>
<td>0.6</td>
<td>40</td>
<td>1.3</td>
<td>-30</td>
</tr>
<tr>
<td>Wegener and co-workers [9]</td>
<td>DLW</td>
<td>1</td>
<td>$\sqrt{2}$</td>
<td>$\sqrt{2}$</td>
<td>0.6</td>
<td>12</td>
<td>1.7</td>
<td>-6</td>
</tr>
<tr>
<td>Chichkov and co-workers [61]</td>
<td>DLW</td>
<td>1</td>
<td>$\sqrt{2}$</td>
<td>$\sqrt{2}$</td>
<td>0.56</td>
<td>8</td>
<td>1.6</td>
<td>-1</td>
</tr>
<tr>
<td>Misawa and co-workers [10]</td>
<td>DLW</td>
<td>2</td>
<td>5.6</td>
<td>2.8</td>
<td>0.6</td>
<td>14</td>
<td>2.1</td>
<td>-0.1</td>
</tr>
</tbody>
</table>

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. 7.6a. The spectrally observed stop band at 1.306 $\mu$m closely matches the predicted stopband between the 5$^{th}$ and 6$^{th}$ bands at 1.304 $\mu$m ($a/\lambda = 0.5$) in the $\Gamma$-Z direction of the energy dispersion curve. The observed $\sim 20$-nm (FWHM) bandwidth exceeds the predicted bandwidth of $\sim 12$-nm possibly due to the apodization effect described above for slightly decreasing filling fraction from top to bottom of the structure.

7.5 Comparison of proposed 3D fabrication techniques

Though all diffractive optics techniques are based on near-field Talbot self-imaging phenomenon, there are significant similarities and differences between four proposed 3D fabrication techniques. Table 7.2 compares four fabrication techniques presented in Chapter 6 and Chapter 7. The 1D-DOE creates a 2D diffraction pattern and interlacing of two such orthogonally rotated 2D patterns created the periodic 3D structure. The phase-tunable DOE as well as both binary and three-level 2D DOEs directly create the 3D diffraction pattern. Hence, the 1D-DOE method needed double laser exposure whereas the other two methods
only required a single laser exposure to fabricate 3D structures. In the 1D-DOE based double
exposure method, a quarter period \( c/4 \) shift between two 2D structures is provided by
physical displacement of DOE with respect to the sample between two laser exposures to
fabricate diamond-like structure. In phase-tunable and three-level DOE methods, this shift
is controlled by the relative phase of diffracted beams. Hence, the double exposure method
is highly susceptible to alignment inaccuracy between the two DOEs. This alignment dif-
ficulties have been reduced in phase-tunable method where a static laser exposure through
precisely separated back-to-back connected phasemasks is used to fabricate 3D structures.
However, a precise separation between two back-to-back connected phasemasks is needed in
order to obtain a specific phase difference. The three-level 2D DOE method is most robust
approach where the phase information is encoded on to a single-surface DOE to form double
basis of a diamond-like structure. The two-level 2D DOE was limited to form only single
basis BCT symmetry structures with much smaller periodicity \( a = b = 570 \text{ nm and } c = 1.84 \mu\text{m} \).
The soft polymer BCT symmetry structures were successfully inverted with silica
to realize robust 3D nanostructures as described in Section 8.3.

For demonstration purposes a DOE period of \( \Lambda = 1.066 \mu\text{m} \) was used in both the 1D-
DOE double exposure method and the phase-tunable DOE method, which resulted in 3D
structures with period \( a = 1.06 \mu\text{m and } c = 6.91 \mu\text{m} \). The optical stopgap for such structures
were observed in the 4 \( \mu\text{m} - 5 \mu\text{m} \) band. Much shorter period of \( \Lambda = 650 \text{ nm} \) for the three-
level 2D-DOE was used which consequently resulted in 3D structures with much smaller
period of \( a = 650 \text{ nm and } c = 2.46 \mu\text{m} \) with stopgap shifted to the 1.25 \( \mu\text{m} - 1.6 \mu\text{m} \) telecom
band. These narrow and strong telecom band stopgaps were used in demonstration of optical
sensing in Section 8.2.1.
### Table 7.2: Comparison between four diffractive optics lithography techniques.

<table>
<thead>
<tr>
<th>Property</th>
<th>1D-DOE</th>
<th>Phase-tunable DOE</th>
<th>2D DOE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diffraction pattern</strong></td>
<td>2D periodic</td>
<td>3D periodic</td>
<td>Binary</td>
</tr>
<tr>
<td><strong>Pattern symmetry</strong></td>
<td>TTR</td>
<td>BCT ⇔ TTR</td>
<td>BCT</td>
</tr>
<tr>
<td><strong>Laser exposure</strong></td>
<td>double</td>
<td>single</td>
<td>single</td>
</tr>
<tr>
<td><strong>Crystal basis</strong></td>
<td>double</td>
<td>single ⇔ double</td>
<td>single</td>
</tr>
<tr>
<td><strong>Shift (S = c/4) control</strong></td>
<td>physical movement</td>
<td>phase control</td>
<td>none</td>
</tr>
<tr>
<td><strong>DOE alignment</strong></td>
<td>need accurate control</td>
<td>moderately robust</td>
<td>robust</td>
</tr>
<tr>
<td><strong>Laser polarization</strong></td>
<td>linear</td>
<td>linear/circular</td>
<td>circular</td>
</tr>
<tr>
<td><strong>Demonstrated 3D period</strong></td>
<td>$a = 1.06 , \mu m$</td>
<td>$a = 1.06 , \mu m$</td>
<td>$a = 570 , \text{nm}$</td>
</tr>
<tr>
<td></td>
<td>$c = 6.91 , \mu m$</td>
<td>$c = 6.91 , \mu m$</td>
<td>$c = 1.84 , \mu m$</td>
</tr>
<tr>
<td><strong>Demonstrated 3D layers</strong></td>
<td>10</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td><strong>Observed stopgap Γ-Z</strong></td>
<td>4 , \mu m - 5 , \mu m</td>
<td>4 , \mu m - 5 , \mu m</td>
<td>-</td>
</tr>
<tr>
<td><strong>Γ-Z stopband strength</strong></td>
<td>-1.5 dB</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Sensing with stopgap shift</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Inversion</strong></td>
<td>-</td>
<td>-</td>
<td>silica</td>
</tr>
</tbody>
</table>

### 7.6 Discussion

In this chapter, single laser exposure fabrication of 3D nanostructures using two types of 2D diffractive optics have been presented. Rogers and coworkers [14] were first to demonstrated the formation of 3D periodic structures in photoresist using 2D binary DOEs. However, they could only fabricate a single basis structure with body-centred-tetragonal (BCT) symmetry using two-level 2D DOEs. In the present work we also demonstrated fabrication of highly uniform single basis BCT symmetry structures with much smaller periodicity ($a = 570 \, \text{nm}$ and $c = 1.84 \, \mu m$) using a two-level square lattice 2D DOE as compared to Rogers group demonstrations of $a = 600 \, \text{nm} - 1 \, \mu m$ and $c = 2 \, \mu m - 3 \, \mu m$. However, we were first to propose and demonstrate a single laser exposure method of fabricating diamond-like photonic crystals by the three-level DOE. 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. 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 nanostructures 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 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 Section 4.3. 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 ($n_b$) [36] according to the generic design guidelines presented in Chapter 4.
Chapter 8

Applications of polymer 3D periodic structures

8.1 Introduction

The present work has provided a wide range of 3D periodic nanostructures with uniform optical and structural properties over large sample area (~2-3 mm diameter) and through large 15-50 µm thickness with a large number of layers (> 40). The short exposure time and small number of process steps shows promise for scaling to very large volume fabrication, dramatically improving the throughput, quality and structural uniformity of 3D nanostructures, especially over that provided by tedious and costly semiconductor processing technology. Even a flexible fabrication approach like 3D laser direct write becomes unacceptably time consuming when processing sample sizes of only 100 microns. In contrast, diffractive optic lithography approach is a parallel processing method that is easily scalable to generating centimeter-scale 3D nanostructures having large number of layers in several seconds. We are optimistic that the practical merits of this 3D fabrication technique will enable new practical manufacturing methods for optical and MEMS applications of such 3D nanostructures.
8.2 Applications of polymer 3D photonic crystals

One of the applications we are investigating is embedding 3D photonic crystal structures into micro-fluidic channels. This will serve two different purposes. In one application, the embedded 3D structures will enable chromatographic separation of cells using electro-fluorosis and in the other application it will enable optical fluid sensing using stopgap information of these structures. The ultimate goal is to combine these methods for optical detection of biological and chemical species.

8.2.1 Fluid sensing with the shift in stopband

The usefulness of the strong stopbands reported for the woodpile structure shown in Fig. 7.5 has been tested by immersing the open crystal with ethanol while recording the optical transmission spectrum. An 8 µL volume of ethanol (n = 1.34) was uniformly sprayed on a 5 mm x 5 mm sample surface area with a micro-pipette. Figure-8.1 shows the transmission spectrum of the air-filled stopband (t = 0-) and the stopband shifts at first immersion (t = 0+) and various times thereafter (2 to 24 min) as the solvent evaporates. The stopband nearly disappears on first immersion, and then recovers by shifting from ~1.26 µm wavelength back to the original stopband (λ₀ = 1.3 µm) after complete evaporation. The stopband shifting speed can be controlled with the volume of ethanol used to fill the open 3D crystal volume.

Contrary to simple Bragg considerations, the stopband shift to shorter wavelength in the presence of ethanol is unexpected and may be due to anomalous dispersion of the higher order stopbands (the stopband is between 5th and 6th band). Nevertheless, the open structure of the present 3D diamond-like films offer strong and narrow stopbands that are attractive for optical sensing application. Such sensing structures can be integrated with cavities
and waveguides for new micro-sensing applications and would thus benefit from the more reproducible and higher volume 3D fabrication method introduced in this research work.

8.2.2 Integration with opto-fluidic channels

The 3D periodic nanostructures can be embedded inside opto-fluidic channels using different laser fabrication techniques combining with conventional semiconductor and soft lithographic techniques. However, a single laser exposure simultaneous fabrication of 3D structures as well as micro-fluidic channels is more attractive from ease of fabrication and integration purposes. We demonstrated a shadow masking technique to define micro-fluidic channels inside 3D structures fabricated by diffractive optic lithography method. The photoresist layer ($n_r$) is exposed through a combination of diffractive phase element ($n_d$) and amplitude mask ($n_{AM}$) as shown in Fig. 8.2 where $n_i$ represent the index matching fluid and $n_s$ is the substrate. The diffractive phase element defines the 3D periodic structure and the amplitude mask shown in Fig. 8.2b defines the open space (i.e. fluidic channels, reservoirs etc.) on the
Figure 8.2: (a) Laser exposure setup for single laser exposure fabrication of 3D periodic structure and micro-fluidic channels using a combination of diffractive and amplitude mask and (b) an amplitude mask for preferential masking of diffracted light to define open channels. Two layers of index matching medium ($n_i$) have been used between DOE substrate ($n_s$) and amplitude mask ($n_{AM}$) and also between amplitude mask and photoresist ($n_r$) layer which is spun onto a substrate of refractive index $n_s$.

sample surface by preferential masking of the diffracted light. For a negative photoresist like SU-8, opaque regions of amplitude mask become open space and transparent regions become polymerized 3D structures after development of the photoresist.

As a demonstration, a 2D binary phase DOE which has been introduced in Chapter 4 has been used in combination with an amplitude mask shown in Fig. 8.2b to expose a photoresist layer (SU-8, $n_r = 1.6$) of thickness $\sim 30 \mu m$ through index matching layers ($n_i = 1.6$) using the same argon ion laser of wavelength 514 nm. The periodicity of the 2D DOE is $\Lambda_x = \Lambda_y = 570 \text{ nm}$ and the line width of the amplitude mask is 50 $\mu m$, which was drawn on a plastic transparent slide using a high resolution laser printing. Figure 8.3a depicts the exposed and developed photoresist layer showing embedded micro-fluidic channel inside a large area 3D photonic crystal structure. A porous 3D photonic crystal structure of BCT symmetry is clearly visible in Fig. 8.3b as expect for a binary 2D DOE.

The present results show possibility of fabrication of 3D photonic crystals embedded
inside micro-fluidic elements using single laser exposure step. These embedded 3D structures can be used for separation of cells and in the other application they can be used for probing cells optically using bandgap information of these structures as demonstrated in Section 8.2.1. However, a different DOE and amplitude mask layout is needed in order to define solid side walls of these open channels. The present combination creates channels inside a matrix of 3D structure without defining a solid side walls which does not efficiently confine the fluid flow through the porous photonic crystal structure. Nevertheless, this shadow masking technique is attractive in single laser exposure fabrication of 3D structures as well as micro-fluidic channels/reservoirs in a opto-fluidic chip.

8.3 Inversion of polymer 3D structures

Inversion of periodic polymer nanostructures plays two important roles. Inversion with a high refractive index material is absolutely necessary in order to realize a complete photonic
bandgap. The inversion process also highly beneficial in converting a soft polymer structure to a more durable robust structure. Ozin and co-workers has demonstrated that polymer 3D periodic structures can be inverted with silica (SiO$_2$) using chemical vapor deposition (CVD) technique [16]. Silica inversion is attractive in converting a “soft” SU-8 structure to a “robust” structure made with a “hard” material. Silica is also attractive for bio-compatibility. Moreover, silica inverted structures can be used as a “hard” template for silicon double inversion using high temperature CVD [16] for complete bandgap device.

Due to large area uniformity of the single basis BCT symmetry structure produced by the commercial two-level 2D-DOE of periodicity $\Lambda_x = \Lambda_y = 570$ nm (Section 7.3.1), this structure was chosen for inversion. The 3D structure was fabricated in SU-8 photoresist using single laser exposure of the 2D DOE and has been shown in Fig. 7.4.

### 8.3.1 Silica coating using chemical vapor deposition

The silica chemical vapor deposition has be performed in collaboration with my colleague Nicole Zacharia in Geoffrey Ozin group. For the deposition of silica (SiO$_2$) using CVD, the polymer (SU-8) sample surfaces were first coated with a thin layer of water (H$_2$O) by bubbling nitrogen gas through water, and into the polymer sample. Next, using silicon tetrachloride (SiCl$_4$) as the precursor, silica was deposited on the sample surface. The chemical reaction $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$ only takes place at the sample surfaces which leads to the layer-by-layer growth of dense, amorphous SiO$_2$ on the sample surfaces while releasing HCl as a byproduct. The process is automatically terminated when the water is consumed [62]. This sequence is repeated until the desired thickness of the silica layer is reached.

For silica coating of the polymer structure shown in Fig. 7.4, the N$_2$ flow of 300 sccm
was directed through a bubbler filled with twice-distilled H₂O for 7 min, leading to a water layer on the polymer sample surfaces. Subsequently, the CVD chamber was flushed with N₂ for 5 min. Then, the N₂ flow was directed for 10 min through a bubbler containing SiCl₄ (Sigma-Aldrich 13736, > 99 %), which led to the layer-by-layer growth of silica on polymer sample surface as shown in Fig. 8.4a-b. The sequence was repeated 3 times here in order to deposit a 100-120 nm thick silica shell around the polymer structure.

8.3.2 Reactive ion etching of silica over-layer

The inner SU-8 “mother” template was removed to create a pure silica structure. To facilitate removal of the inner SU-8 structure, first the top surface of the SiO₂ over-layer was removed by RIE in an SF₆ plasma (etch time = 20 min, SF₆ gas pressure = 22 mTorr and gas flow rate = 40 sccm, RIE power = 70 W) (Trion Ltd., Phantom Etcher RIE-ICP system) to exposure SU-8 structure for subsequent polymer etching step. Figure 8.4c-d shows SEM images of top and cross-sectional view of the structure after the SiO₂ over-layer removal step.

8.3.3 Polymer template removal using reactive ion etching

The SU-8 template can be removed either by reactive ion etching using O₂ plasma or by high temperature (∼450°C) calcination of SU-8 [16]. We found high temperature calcination to be a more aggressive process and responsible for frequent 3D structural collapse. Instead the SU-8 template was removed by gentle pure O₂ plasma etching (etch time = 3.5 hr, O₂ gas pressure = 50 mTorr, O₂ gas flow rate = 60 sccm and RIE power = 15 W). Figure 8.4e-f shows SEM images of cross-sectional views of the focused ion beam (FIB) milled structure. The SiO₂ shells arranged on BCT point lattice can be clearly observed as expected after removal of the SU-8 template. The quality of the SiO₂ inversion can be gauged from energy-
Figure 8.4: Top (a) and cross-sectional (b) SEM images of SiO₂ coated BCT symmetry structure. (c) and (d) corresponding top and cross-sectional views after SiO₂ over-layer removal. (e) FIB milled cross-section after removal of SU-8 template and the corresponding enlarged cross-sectional view is shown in (f). EDX spectra (g) and material composition (h) showing ∼90% presence of SiO₂ in the inverted structure.

dispersive X-ray spectroscopy (EDX) data given in Fig. 8.4g-h, confirming ∼90% (weight) presence of SiO₂.

8.3.4 Optical characterization of silica inverted structures

The $c/a = 1.54/0.57 = 2.7$ ratio of the present single basis BCT symmetry structure is still large as well as the refractive index of the photoresist ($n_r = 1.6$) is too small to create photonic stopgaps of the polymer BCT symmetry structure. However, stopgaps are predicted for the
Figure 8.5: Normalized transmission spectrum measured as normal angle of incidence through the structure in Fig. 8.4e showing a strong (-28 dB) stopband at 1.296 µm.

SiO$_2$ inverted structure shown in Fig. 8.4e along several crystallographic directions. The sample shown in Fig. 8.4e was optically probed along the Γ-Z direction (c axis in Fig. 7.4c) with a broad band source in the 1.25 µm to 1.65 µm spectral range, providing the normalized transmission spectrum shown in Fig. 8.5. All spectral recordings were normalized against a reference spectrum recorded through an identical substrate coated with an identical SiO$_2$ coating of ~30 µm thickness. At 1.296-µm wavelength, a strong -28 dB attenuation stopband with narrow response of ~10 nm (FWHM) is observed.

The strong and narrow stopband (~10 nm) indicates that all 22 layers in Fig. 8.4e-f are collectively acting as coherent planes indicating formation of a highly uniform silica inverted 3D structure throughout the thick structure (30 µm) and over large area (2 mm diameter), which would otherwise be washed out by minor lattice distortions for such narrow high-order bands.
8.4 Summary

In summary, it has been demonstrated that strong and narrow stopgaps of polymer 3D photonic crystal structures fabricated by diffractive optics lithography technique can be used in optical sensing applications. These 3D structures have been integrated into micro-fluidic channels using shadow masking of the diffraction pattern. The polymer structures have been effectively inverted with silica using chemical vapor deposition technique to convert a “soft” polymer structure to a “robust” structure made with a “hard” material. The high quality silica inverted structure promises possible use in biological sensing applications as well as possible silicon double inversion for fabricating silicon 3D photonic crystals.
Chapter 9

Conclusion and future work

In Section 9.1, the present work has been compared with other published results in literature. In Section 9.2, the significant scientific and engineering contributions of this thesis are discussed. The dissertation is concluded with a outline for future work in Section 9.4.

9.1 Comparison with other literature results

Rogers and coworkers were first to demonstrate formation of 3D periodic structures in photoresist using binary 2D DOEs [14]. However, as pointed out in Section 4.4.3.4, a binary 2D-DOE produces a single basis BCT symmetry diffraction pattern. Hence, 3D structures reported by Rogers group remain restricted to only single-basis BCT symmetry structures with lateral period \((a)\) reported to be between 600 nm and 1 \(\mu m\) [14, 63, 64]. In the present work, we also demonstrated fabrication of highly uniform single basis BCT symmetry structures with much smaller periodicity \((a = b = 570 \text{ nm} \text{ and } c = 1.84 \mu m)\) using a two-level square lattice 2D DOE. The soft polymer BCT symmetry structures were successfully inverted with silica to realize robust 3D nanostructures in Section 8.3.

Lin et al. extended DOEs to the fabrication of 3D “Woodpile”-type photonic crystal templates in photoresist by double exposures of orthogonal 1D-DOEs [15]. In the present thesis,
the fabrication precision was improved and the first spectral characterization of woodpile photonic crystal templates formed by double laser exposure method was made [43]. Recently, Chen and co-workers demonstrated fabrication of orthorhombic 3D structure using the same double exposures method but with 60° rotated 1D-DOEs to interlace two 2D structures with 60° angle [65]. To overcome the inherently imprecise DOE alignment that arises between two laser exposures, we were first to devise a single laser exposure 3D periodic structure fabrication method 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 [35]. We subsequently demonstrated use of circularly polarized light for the first time to balance the diffraction order efficiencies and improve the structural uniformity [55]. Although, the phase tunable near-field DOE method is versatile, it requires accurate phase control for fabrication of diamond-like structure.

John and co-workers proposed a phasemask design based on orthogonal placement of linear phasemasks on opposite surfaces of a single DOE substrate [56]. This requires tedious etching and deposition processes on opposite surfaces of a substrate as well as precise control of separation between two 1D gratings. We presented 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 [36]. Rather than rely on the precise control of substrate thickness [56], or the accurate physical separation of two DOEs for phase control [35], a phase shift was built into the single-surface DOE design. This enabled ease of etch of diffractive elements on single side of a substrate. This new multi-level DOE design permitted a large number of layers (> 40) to form in thick photoresist, generating a record
strength -30 dB stopband at 1.306 µm telecom band. The usefulness of this stopband for refractive index sensing of liquids has been demonstrated.

9.2 Significance of the present work

The present work demonstrated a simple 3D fabrication technique where 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 DOE fabrication is easily scalable to high volume and large area manufacturing of highly uniform 3D photonic crystals. The biggest contribution of the present work is demonstration of novel phase control mechanisms to control near-field diffraction pattern. The phase control permitted the first single exposure near-field lithography based fabrication of the diamond-like structure. The phase control 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. The present work has provided 3D periodic nanostructures with uniform optical and structural properties over large sample area (≈3-4 mm diameter) and through large 15-50 µm thickness with large number of layers (> 40) having period of 550 nm to 1 µm and feature sizes between 100 nm and 400 nm. Photographs of one such large area uniform 3D sample which was fabricated using phase-tunable diffractive optics method, are shown in Fig. 9.1. Figure 9.1a-d were taken with different viewing angles where four different viewing angles manifested as four different sample colors. The top SEM view of the sample is shown in Fig. 9.1e.

The refractive index of the photoresist was too small to create a complete photonic bandgap. However, the presence of stopgaps were demonstrated for the woodpile structure
Figure 9.1: The photograph of a large area uniform 3D sample with four different viewing angles (a)-(d). (e) top SEM view of the sample.

along several crystallographic directions. SEM and spectral observations indicated 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 was demonstrated by spectral shifts of stopband under liquid immersion. Such sensing structures can be integrated with cavities and waveguides for new micro-sensing applications and would thus benefit from the more reproducible and higher volume DOE fabrication method introduced in this thesis. The soft polymer structures were successfully inverted with silica to realize robust 3D nanostructures. We are optimistic that the practical merits of this 3D fabrication technique will enable new practical manufacturing methods for optical and MEMS applications of 3D nanostructures. This dissertation has advanced the diffractive optics based lithography technique to fabricate a wide range of three-dimensional periodic nanostructures in a simple but robust way.

9.3 Conclusion

In summary, a diffractive optics lithography based 3D periodic structure fabrication technique has been presented. The method is robust and simple to align unlike other 3D fabrica-
tion techniques. The present work started with one-dimensional diffractive optics for double and single laser exposure fabrication of 3D periodic structures. However, imprecise alignment between two DOE exposures prevented double exposure method from reproducibly generate 3D structures and a single exposure DOE method was therefore preferred for improved uniformity and reproducibility. The phase-tunable DOE enabled DOE formation of 3D photonic crystal templates with a single laser exposure step. The controlled separation of the two optical elements provided a variable phase shift to manipulate the interlacing position of two orthogonally rotated periodic structures, and thereby facilitated fabrication of diamond-like woodpile structures having tetragonal symmetry through to structures having body-centered-tetragonal symmetry, and including variations in between. Although, the phase tunable DOE method was versatile, it required accurate phase control in order to provide a quarter period shift between two orthogonal interference patterns required for diamond-like structure. To improve fabrication reproducibility of diamond-like structure, a single-surface specially designed three-level DOE was proposed with locked-in phase-shift optimized for formation of diamond-like photonic crystal structure in a single laser exposure step. The three-level single-surface DOE was laser fabricated on a thin polymer film by two-photon polymerization. Diamond-like structures were fabricated in photoresist having Γ-Z (normal incidence) stopbands now shifted into the 1.25-1.65 \( \mu m \) telecom band [36] from previous observations in the 3 to 5 \( \mu m \) range [43]. 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 \( \mu m \). The usefulness of this stopband for refractive index sensing of liquids has been demonstrated. The soft polymer structures were successfully inverted with silica to realize robust 3D nanostructures. The high quality silica inverted structure promises
possible use in biological sensing applications as well as possible silicon double inversion for fabricating silicon 3D photonic crystals.

Three-dimensional periodic structure were consistently fabricated over large sample area (∼2 mm diameter) and through large 10 - 30 µm thickness. The rapid exposure time (∼5-10 s) and small number of process steps shows promise for scaling to very large volume fabrication, dramatically improving the throughput, quality and structural uniformity of 3D nanostructures, especially over that provided by tedious and costly semiconductor processing technology. Even a flexible fabrication approach like 3D laser direct write becomes unacceptably time consuming when processing sample sizes of only 100 microns. In contrast, diffractive optics lithography is a parallel processing method that is easily scalable to generating centimeter-scale 3D photonic crystals in several seconds when using high power lasers and beam scanning exposure techniques.

9.4 Future directions

During this research work many scientific and technical difficulties have been encountered and many of them systematically solved. However, quite a few technical directions remained to be explored as listed below as future research directions.

1. Woodpile structure with complete bandgap

A polymer woodpile template fabricated according to the design guidelines given in Section 4.3 will demonstrate a complete bandgap after inversion with a high refractive index material. The complete bandgap is necessary in order to manipulate photons to fabricate interesting optical devices like filters, lasers, resonators, splitters. The
complete bandgap is also necessary for highly functional integrated photonic chips and for the application of photonic bandgap properties to optical quantum information processing. In the diffractive optics method, the first step will be to fabricate a multi-level DOE using high refractive index materials. Then the fabricated polymer structure can be inverted with a high refractive index material like silicon. The process steps to fabricate a woodpile structure with complete bandgap are listed below:

- Three-level DOE fabrication according to the design guidelines given in Section 4.3 using high refractive index materials.

- Suitable exposure laser to define lattice constants \((a\) and \(c\)) of the woodpile structure so that bandgap location can be tuned to a desired range. For example, if the exposure laser wavelength is \(\lambda_d = 514\) nm, the maximum bandgap condition \(\lambda_d/\Lambda = 1.57\) will create complete bandgap centred around \(\lambda = 650\) nm. A longer wavelength exposure laser is needed for a bandgap in the telecom band.

- The polymer 3D template can be inverted with silica according to the process steps given in Section 8.3. Silica inversion is attractive in converting a “soft” polymer structure to a “robust” structure made with a “hard” material. The silica inverted structures can then be used as a “hard” template for silicon (double) inversion using chemical vapor deposition technique [16].

2. Defect creation inside 3D periodic structures

For functionalization of 3D periodic structures, an engineered “defect” may be incorporated inside a perfectly periodic structure. However, the Talbot effect always creates
a periodic diffraction pattern and hence, direct incorporation of defect seems impossible in diffractive optics lithography. One possible solution is combining direct laser writing [66, 67] with DOE exposure. First the photoresist must be exposed with direct laser writing to define a defect and subsequently the same photoresist layer must be exposed through a DOE to define a 3D periodic structure. However, accurate alignment is needed in order to register the defect in a precise location within the 3D periodic pattern.

3. Integration of 3D nanostructures with micro-fluidic chips

The embedded 3D structures can be used for separation of cellular contents and in the other application they can be used for probing cells optically using bandgap information of these structures. The present results in Section 8.2.2 showed possibility of fabrication of 3D photonic crystals embedded inside micro-fluidic elements using single laser exposure step. However, a different DOE and amplitude mask layout is needed in order to define solid side walls of these open channels. The present combination created channels inside a matrix of 3D structure without defining a solid side wall which does not efficiently confine the fluid flow through the porous photonic crystal structure.
Appendix A

Appendix-Derivation of Talbot length from interference equations

The physical origin of Talbot self-images in the near-field or Fresnel region is the result of addition of all diffraction orders with their phase delay differences equal to or integer multiple of $2\pi$ [68, 69]. Figure- A.1 shows ray-optics picture of interference of different diffracted beams of a normally illuminated grating inside a medium of refractive index ($n_r$) placed in the Fresnel or near-field of the grating. The complete derivation of Talbot length from interference equations assuming that only the three central diffraction orders ($m = -1, 0, 1$) are propagating waves, i. e., $1 < \Lambda/\lambda_m \leq 2$, has been given below. Propagation constants inside the medium are given in Eq. (A.1).

$$
\begin{align*}
K_0 &= \frac{2\pi n_r}{\lambda_d} [0 \ 0 \ 1] , \\
K_1 &= \frac{2\pi n_r}{\lambda_d} [\sin \theta_r \ 0 \ \cos \theta_r] , \\
K_{-1} &= \frac{2\pi n_r}{\lambda_d} [-\sin \theta_r \ 0 \ \cos \theta_r] \\
\end{align*}
$$

where $\lambda_d$ is the free space wavelength, $n_r$ is the refractive index of the medium and $\theta_r$ is the first order beam diffraction angle inside the medium. The diffraction angle $\theta_r$ can be related to laser wavelength ($\lambda_d$) and grating period ($\Lambda$) by snell’s law and law of diffraction as

$$
\sin \theta_r = \frac{n_i}{n_r} \sin \theta_i = \frac{n_i}{n_r} \frac{\lambda_d}{n_r \Lambda} = \frac{\lambda_d}{n_r \Lambda} \quad (A.2)
$$

The Talbot self-imaging condition is:
where \( m \) is an integer and \( r \) is the space co-ordinate. Now combining Eq. (A.1) and Eq. (A.3) gives,

\[
\frac{2\pi n_r}{\lambda_d} [-\sin \theta_r x + (1 - \cos \theta_r) z] = 2\pi m \quad (A.4)
\]

\[
\frac{2\pi n_r}{\lambda_d} [\sin \theta_r x + (1 - \cos \theta_r) z] = 2\pi m \quad (A.5)
\]

Solving Eq. (A.4) and Eq. (A.5) for space co-ordinate \( z \) gives,

\[
z = \frac{2\pi m}{(K_{0z} - K_{-1z})} = \frac{m\lambda_d/n_r}{(1 - \cos \theta_r)} \quad (A.6)
\]

Solution of \( z \) for two consecutive integer \( m = 1 \) and \( m = 2 \) are:

\[
z_1 = \frac{2\pi}{(K_{0z} - K_{-1z})} = \frac{\lambda_d/n_r}{(1 - \cos \theta_r)} ; \quad z_2 = \frac{4\pi}{(K_{0z} - K_{-1z})} = \frac{2\lambda_d/n_r}{(1 - \cos \theta_r)} \quad (A.7)
\]

The Talbot length \((Z_{Tg})\) is defined as distance between two consecutive points of constructive interference along the optical axis \((z\text{-axis})\) and hence it is defined as,
\[
Z_{TG} = (z_2 - z_1) = \frac{2\pi}{(K_{0z} - K_{-1z})} = \frac{\lambda_d/n_r}{(1 - \cos \theta_r)} = \frac{\lambda_d/n_r}{(1 - \sqrt{1 - \sin^2 \theta_r})}
\]  

(A.8)

Now replacing Eq. (A.2) into Eq. (A.8) we get the final expression for generalized Talbot length \((Z_{TG})\) as given in Eq. (A.9).

\[
Z_{TG} = \frac{\lambda_d/n_r}{1 - \sqrt{1 - \left(\frac{\lambda_d}{n_r \Lambda}\right)^2}}
\]  

(A.9)
Appendix B

Appendix-Photoresist sample preparation

B.1 Recipe for photoresist sample preparation

Preparing good quality photoresist samples is extremely critical in producing high quality 3D structures in a reproducible manner. During this research work a recipe has been developed for SU-8 sample preparation for high quality 3D structure fabrication using CW laser at $\lambda_0 = 514$ nm wavelength.

B.1.1 Chemicals required

The chemicals required for sample preparation are listed below:

- SU-8-2050 (From MicroChem)
  - Purpose: photosensitive material.

- H-NU 470 (From Spectra group limited): Typical range 0.1% - 0.5% weight of SU-8.
  
  For relatively low power exposure higher H-NU 470 concentration (0.4%-0.5% weight of SU-8) is required to avoid long exposure time. H-NU 470 should be kept in a dry moisture free place.
- Purpose: Photo initiator to increase photosensitivity of SU-8 at 514 nm. Since SU-8 is optimized for i-line exposure (≈365 nm), photo-initiator is needed to improve SU-8 absorption at 514 nm.

- **TEA (Thriethylamine) (From ACP, Montreal):** Typical range 0.2-0.3 molar ratio of H-NU weight. For high resolution 3D fabrication (TEA: H-NU) mol ratio of (0.3:1) is used which is equal to TEA amount = 7.99 μL for 0.5% of H-NU 470 concentration considering molar weight of TEA = 101.1g/mol, molar weight of H-NU 470 = 520g/mol and density of TEA = 0.73g/ml.

- Purpose: Reduces photosensitivity to background light for fabrication of porous 3D structures. However, use of TEA is optional. Details of use of TEA can be found in Ref. [70].

- **OPPI (From Spectra group limited):** 2.5% weight of SU-8. OPPI has a shelf life of maximum 6 months and should be kept in a dry moisture free place.

- Purpose: Photo co-initiator works in conjunction with H-NU 470.

- **DMMA (N, N-dimethylacryl-amide-99%) (From Aldrich):** Need enough amount to dissolve H-NU 470 and OPPI.

- Purpose: Solvent to dissolve H-NU 470 and OPPI.

- **Omnicoat (from MicroChem):** 6-8 ml for 25-30 samples (enough to completely coat the surface of the glass substrates).

- Purpose: Improve adhesion between photoresist layer and glass substrate.
B.1.2 Cutting and cleaning glass substrates

Regular microscope slides are cut into square shapes of 1 in x 1 in. Substrates are cleaned with Piranha (a mixture of sulfuric acid ($H_2SO_4$) and hydrogen peroxide ($H_2O_2$)) to remove organic substances, dart etc.

B.1.3 Photoresist mixture preparation

- Use opaque bottles as containers to prevent strong penetration of visible light.

- Weigh H-NU 470 using a digital balance on weighing paper. Transfer H-NU 470 to the opaque bottle and add an adequate amount of DMMA such that the H-NU 470 is submerged. Use magnetic stirring to dissolve H-NU 470 into DMMA for approximately 1 hr. Try to place chemicals in the center of the bottom not to leave them on the wall by accident. Avoid fast stirring to minimize splashing of solution to the sides of the bottle.

- (Optional) Add TEA to the H-NU 470 + DMMA solution using a micro pipette. Need to ensure all of the TEA is added by touching the side of the container with the pipette needle close to the solution surface.

- Add OPPI to the H-NU 470 + DMMA + TEA solution. Need to add some more DMMA to submerge the OPPI. Stir the mixture for Approx. 1 hr until it becomes homogeneous mixture.

- Add 25% of total SU-8 to the H-NU 470 + DMMA + TEA + OPPI mixture and stir for 6-8 hrs till it becomes a homogeneous mixture. Add remaining 75% of SU-8 to the mixture and stir for 24 hours or more as required till it becomes a transparent
homogeneous mixture. Place a drop of the formulated photoresist between glass slides and view it vertically in a light source such as an overhead projector or flashlight. The presence of any undissolved orange particles is an indication of incomplete solubility.

B.1.4 Spin-coating and baking

A uniform layer of SU-8 is spin coated on glass substrate following steps below:

- Dry piranha cleaned glass substrates with \( N_2 \) gas or dry air and bake them @ 200 deg C for 2-3 in. Keep them inside new plastic containers.

- Spin Omnicoat using two steps spin cycles of 500 rpm for 5s with acceleration 108 rpm \(/s^2\) and then 3000 rpm with acceleration 324 rpm \(/s^2\) for 30s. Bake substrate at 200° C for 2 minutes.

- Spin a thick photoresist layer (~30 micrometers) using spin cycles of 500 rpm for 5s with acceleration 108 rpm \(/s^2\) and then 3000 rpm for 50s with acceleration 324 rpm \(/s^2\). Bake the thick photoresist sample at 65°C for 3 minutes and then at 95°C for 10 minutes. Keep samples away from visible light.

It has been observed that photosensitivity of H-NU 470 added SU-8 deteriorates with time. One week time span between sample preparation and laser exposure has been found to be optimal for producing high quality reproducible 3D structures.
Bibliography


