RICE UNIVERSITY

Photonic Crystals at Visible, X-ray, and Terahertz Frequencies

by

Tushar Prasad

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Daniel M. Mittleman
Associate Professor, Chair
Electrical and Computer Engineering

Vicki L. Colvin, Professor
Chemistry

Michael S. Wong, Associate Professor
Chemical and Biomolecular Engineering

HOUSTON, TEXAS

NOVEMBER 2007
INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.
ABSTRACT

Photonic Crystals at Visible, X-ray, and Terahertz Frequencies

by

Tushar Prasad

Photonic crystals are artificial structures with a periodically varying refractive index. This property allows photonic crystals to control the propagation of photons, making them desirable components for novel photonic devices. Photonic crystals are also termed as "semiconductors of light", since they control the flow of electromagnetic radiation similar to the way electrons are excited in a semiconductor crystal. The scale of periodicity in the refractive index determines the frequency (or wavelength) of the electromagnetic waves that can be manipulated.

This thesis presents a detailed analysis of photonic crystals at visible, x-ray, and terahertz frequencies. Self-assembly and spin-coating methods are used to fabricate colloidal photonic crystals at visible frequencies. Their dispersion characteristics are examined through theoretical as well as experimental studies. Based on their peculiar dispersion property called the superprism effect, a sensor that can detect small quantities of chemical substances is designed. A photonic crystal that can manipulate x-rays is fabricated by using crystals of a non-toxic plant virus as templates. Calculations show that these metallized three-dimensional crystals can find utility in x-ray optical systems. Terahertz photonic crystal slabs are fabricated by standard lithographic and etching techniques. In-plane superprism effect and out-of-plane guided resonances are studied by terahertz time-domain spectroscopy, and verified by numerical simulations.
ACKNOWLEDGMENTS

There are various people who have contributed towards the completion of this thesis. First, I would like to acknowledge the support and guidance of my advisors, Professor Vicki Colvin and Professor Daniel Mittleman. It was a rewarding experience to work in an interdisciplinary environment, and acquire skills that span not just physics but several other fields of applied science. I am thankful to Professor Michael Wong for giving me feedback on my research, and Professor Bruce Johnson for always willing to discuss various academic issues pertaining to my career.

I would like to thank Professor Tianwei Lin and Dr. Joshua Falkner for their collaboration in the virus crystal project, and Professor Peng Jiang and Christopher Corbet for their assistance in the analysis of spin-coated colloidal crystals. Dr. Myung Kim was helpful in letting me use the plasma etcher in his lab. Colloidal particles prepared by Dr. Junyan Zhang and Silvia Rubio were useful in some of the projects that I worked on. Dr. Rajesh Rengarajan was always interested in discussions on various research projects. Patrick Johnson would make himself available even during the weekends to manage issues relating to the clean room. I am also thankful to Dr. Zhongping Jian, with whom I worked on the terahertz superprism effect.

Particularly, I am indebted to all the Colvin and Mittleman group students, who have always helped in one way or the other towards getting the research done. Finally, I am very grateful for the encouragement and support of my parents.
# TABLE OF CONTENTS

Abstract........................................................................................................................................... ii  
Acknowledgments.............................................................................................................................. iii  
Table of Contents.............................................................................................................................. iv  
List of Figures..................................................................................................................................... x  
List of Tables..................................................................................................................................... xviii  
Preface................................................................................................................................................ xix  

Chapter 1: Photonic crystals............................................................................................................. 1  
1.1 Basic concept.............................................................................................................................. 1  
1.2 Applications of photonic crystals............................................................................................. 4  
1.3 Historical background................................................................................................................ 6  
  1.3.1 Development in fabrication and theory............................................................................... 7  
1.4 Current methods of fabrication................................................................................................. 10  
1.5 Advanced simulation techniques............................................................................................... 12  
  1.5.1 Plane wave expansion method............................................................................................. 13  
  1.5.2 Finite-Difference Time-Domain method (FDTD)................................................................. 15  
  1.5.3 Finite Element Method (FEM)............................................................................................ 16  
  1.5.4 Transfer matrix method......................................................................................................... 17  
  1.5.5 Applicability of the simulation techniques to photonic crystals....................................... 18  

Chapter 2: Photonic crystals for different frequency regimes....................................................... 21
2.1 Introduction ............................................................................................................. 21
2.2 Terahertz photonic crystals .................................................................................... 22
2.3 Photonic crystals at visible frequencies ................................................................. 26
    2.3.1 Colloidal crystals: fabrication .......................................................................... 27
    2.3.2 Colloidal crystals: properties ........................................................................... 31
2.4 Photonic crystals at x-ray frequencies ................................................................... 34

Chapter 3: Superprism effect in macroporous polymer photonic crystals .............. 36
    3.1 Introduction .......................................................................................................... 36
    3.2 Complete photonic band structure ..................................................................... 39
    3.3 Dispersion surface and propagation direction ...................................................... 40
    3.4 Results and discussion ....................................................................................... 44
    3.5 Conclusion ............................................................................................................ 55

Chapter 4: A photonic crystal sensor based on the superprism effect ......................... 57
    4.1 Introduction .......................................................................................................... 57
    4.2 Numerical modeling .............................................................................................. 59
    4.3 Sensor configuration ............................................................................................. 63
    4.4 Conclusion ............................................................................................................ 65

Chapter 5: Experiment for measuring superprism effect in inverted opals ............... 66
    5.1 Introduction .......................................................................................................... 66
    5.2 Sample fabrication ................................................................................................. 67
5.2.1 Fabrication of samples with sphere diameters greater than 400 nm...........68

5.3 Experimental setup......................................................................................72

5.4 Operation......................................................................................................74

5.5 Results and discussion..................................................................................77

5.6 Conclusion.....................................................................................................80

Chapter 6: Colloidal photonic crystals formed by spin-coating.......................81

6.1 Introduction....................................................................................................81

6.2 Sample fabrication and electron microscopy...............................................83

6.3 Optical spectrum and numerical simulations..............................................89

6.4 Conclusion.....................................................................................................98

Chapter 7: Nanostructured virus crystals as photonic crystals for x-rays..........99

7.1 Introduction....................................................................................................99

7.2 Virus crystal fabrication and characterization..............................................101

7.3 X-ray reflectivity of the CPMV...................................................................103

7.4 Conclusion.....................................................................................................109

Chapter 8: Superprism effect in a terahertz photonic crystal slab.....................110

8.1 Introduction....................................................................................................110

8.2 Superprism experiment..................................................................................111

8.3 Theoretical analysis.......................................................................................114

8.4 Conclusion.....................................................................................................120
Chapter 9: Guided resonances in terahertz photonic crystal slabs..................121

9.1 Introduction........................................................................................................121
9.2 Experiment...........................................................................................................124
9.3 Numerical modeling.............................................................................................126
9.4 Line shape analysis..............................................................................................129
9.5 Dependence of the resonances on the structural parameters.........................131
  9.5.1 Effect of change in the hole radius $r$..................................................131
  9.5.2 Effect of change in the lattice parameter $a$..............................................132
  9.5.3 Effect of change in the $r/a$ ratio..............................................................134
  9.5.4 Effect of change in the slab thickness $t$..................................................138
9.6 Transmission spectrum of crystals with different lattice structures..............146
9.7 Conclusion..........................................................................................................148

Chapter 10: The effect of structural disorder on guided resonances..................150

10.1 Introduction........................................................................................................150
10.2 Experiment...........................................................................................................152
10.3 Effect of disorder in the hole diameter..............................................................155
  10.3.1 Disorder in hole size.................................................................................155
  10.3.2 Disorder in hole shape...............................................................................158
10.4 Effect of disorder in the lattice parameter.......................................................161
10.5 Conclusion..........................................................................................................164
Appendix B: Numerical computation of the super prism effect .................. 215
B.1 Photonic band structure calculation ........................................... 215
  B.1.1 Standard photonic band structure ........................................... 216
  B.1.2 Nature of bands: isotropic and anisotropic .............................. 217
  B.1.3 Complete photonic band structure .......................................... 217
B.2 Dispersion surface and propagation direction calculation ................ 219
  B.2.1 Calculation with respect to {001} set of planes ......................... 222
  B.2.2 Calculation with respect to {111} set of planes ........................ 228
B.3 Summary ...................................................................................... 231

*Scheme* code to calculate the complete photonic band structure (K LW plane) ............ 232
*Scheme* code to calculate the complete photonic band structure (LUW plane) ............ 233
*Scheme* code to calculate the complete photonic band structure (W UX plane) ............ 234
*Matlab* code to generate the full dispersion surface ...................................... 235
*Matlab* code to calculate the super prism effect .......................................... 239
LIST OF FIGURES

Chapter 1: Photonic crystals

Figure 1.1: Schematic of one, two and three-dimensional photonic crystal.................2

Chapter 2: Photonic crystals at different frequency regimes

Figure 2.1: The electromagnetic spectrum.................................................................22
Figure 2.2: Scanning electron micrographs (SEM) showing two- and
three-dimensional terahertz photonic crystals...........................................23
Figure 2.3: Schematic of terahertz time-domain spectroscopy (THz-TDS)...............25
Figure 2.4: Naturally occurring gemstone opal and its crystal lattice structure.........27
Figure 2.5: Schematic of the convective self-assembly process.................................29
Figure 2.6: Thickness control of the colloidal photonic crystals..............................30
Figure 2.7: Normal incidence transmission spectra of the colloidal photonic
crystals, as a function of the sphere diameter.................................................32
Figure 2.8: Normal incidence transmission spectra of the colloidal photonic
crystals, as a function of the film thickness..................................................33

Chapter 3: Superprism effect in macroporous polymer photonic crystals

Figure 3.1: Band structure of the inverted opal photonic crystal.................................41
Figure 3.2: Nature of the photonic band: isotropic and anisotropic...........................42
Figure 3.3: Iso-energy surfaces calculated at three different frequencies....................43
Figure 3.4: Slice through dispersion surface explaining the calculation method........46
Figure 3.5: Computed internal propagation angle as a function of frequency, for an incoming beam incident on \{111\} facet of the photonic crystal.............47

Figure 3.6: Computed dependence of the internal propagation angle on the input angle, at two different frequencies. The beam is incident on the \{001\} facet of the crystal.........................................................49

Figure 3.7: Same as Figure 3.6, but for the \{111\} facet.................................49

Figure 3.8: A close-up view of Figure 3.7, at $\theta_{in} = 45^\circ$, for five closely-spaced frequencies..........................................................50

Figure 3.9: Internal propagation angle as a function of frequency, depicting the sensitivity to small changes in the polymer refractive index ..........51

Figure 3.10: Visual illustration of the out-of-plane propagation..........................53

Figure 3.11: Numerical illustration of the out-of-plane propagation....................54

Chapter 4: A photonic crystal sensor based on the superprism effect

Figure 4.1: Band structure of the inverted opal photonic crystal.........................61

Figure 4.2: Iso-energy surfaces calculated at two different frequencies..................62

Figure 4.3: Schematic of the envisioned superprism sensor..............................63

Figure 4.4: Calculated sensor response for small changes in the refractive index........65

Chapter 5: Experiment for measuring superprism effect in inverted opals

Figure 5.1: Schematic of the convective self-assembly process..........................68

Figure 5.2: Schematic of the procedure for fabrication of macroporous polymer photonic crystals.........................................................68
Figure 5.3: Experimental setup for the sand-bath method.................................70

Figure 5.4: Typical sand-bath samples coated on glass substrates.......................71

Figure 5.5: UV-Vis spectra of samples obtained by the sand-bath .......................72

Figure 5.6: Experimental setup for measurement of the superprism effect...............74

Figure 5.7: A computation of the expected experimental data............................75

Figure 5.8: Experimental data for a crystal made from spheres of diameter 443 nm......78

Figure 5.9: Same as Figure 5.8, but for a different scan range............................79

Chapter 6: Colloidal photonic crystals formed by spin-coating

Figure 6.1: Spin-coated photonic crystals fabricated on glass and silicon wafers........83

Figure 6.2: SEM of the spin-coated crystals. The pair-correlation function from

one of the images suggests that the center-to-center distance is close
to 2.828 \times r.........................................................85

Figure 6.3: Unit cells of the hexagonal ABAB... and the simple cubic lattices.

Ideal arrangement of the top two layers, and the corresponding

SEM image of the spin-coated photonic crystal.................................87

Figure 6.4: Cross-sectional SEM image of the spin-coated photonic crystal..........88

Figure 6.5: Comparison of the cross-sectional SEM image of the spin-coated

photonic crystal with the computer-generated cross-sections of the

simple cubic and hexagonal lattices.............................................88

Figure 6.6: Typical normal incidence reflectivity spectrum (optical density)

of the spin-coated photonic crystal.........................................90

Figure 6.7: First Brillouin zone of the hexagonal lattice...............................91
**Figure 6.8:** Photonic band structure of the hexagonal lattice.................................93

**Figure 6.9:** Photonic band structure of the simple cubic lattice...............................94

**Figure 6.10:** Variation of the filling fraction and c/a, for the hexagonal
ABAB... lattice, as the lattice parameter ‘a’ changes from the
close-packed configuration (a/D=1.0) to the ideal spin-coated
lattice arrangement (a/D=1.414).................................................................95

**Figure 6.11:** Experimental and calculated transmission spectra of the spin-coated
photonic crystals.................................................................97

**Chapter 7: Nanostructured virus crystals as photonic crystals for x-rays**

**Figure 7.1:** Lattice structure of the body-centered-cubic form of the Cowpea
Mosaic Virus (CPMV) crystal.................................................................102

**Figure 7.2:** Transmission electron microscope (TEM) images depicting the
lattice planes of the metallized CPMV crystal........................................103

**Figure 7.3:** Refractive index and dielectric constant of platinum and palladium,
for the wavelength range of 20-50 nm.....................................................105

**Figure 7.4:** Photonic band structure of the platinum infiltrated CPMV crystal.........107

**Figure 7.5:** Computed x-ray reflectivity of the metallized CPMV crystal thin film......108

**Chapter 8: Superprism effect in a terahertz photonic crystal slab**

**Figure 8.1:** Image of the terahertz photonic crystal, and a schematic of the
experimental setup for measurement of the superprism effect.....................112

**Figure 8.2:** Modes of the metal parallel plate waveguide, when air, silicon, or the
Figure 8.3: Measured amplitude spectra of the THz radiation, depicting superprism characteristics. 115

Figure 8.4: Band structure (TM polarization) of the photonic crystal slab, assuming infinite slab thickness. 116

Figure 8.5: Image depicting FDTD calculations of the superprism effect. 118

Figure 8.6: Image depicting FEM calculations of the superprism effect. 119

Figure 8.7: Comparison of the observed superprism effect with various theoretical predictions. 119

Chapter 9: Guided resonances in terahertz photonic crystal slabs

Figure 9.1: A schematic of the experimental setup. 125

Figure 9.2: An image of the photonic crystal slab, and the corresponding normal-incidence transmission spectrum. 125

Figure 9.3: The FEM model for the hexagonal lattice photonic crystal. 128

Figure 9.4: Same as Figure 9.2(b), except that the calculated spectrum is obtained from an analytical model (Equation 9.4). 131

Figure 9.5: Variation of guided resonances with the hole radii $r$. 133

Figure 9.6: Variation of guided resonances with the lattice parameter $a$. 133

Figure 9.7: Shift in the positions of resonances as a function of the $r/a$ ratio. 135

Figure 9.8: Transmission spectra of photonic crystal slabs with same $r/a$ ratio but different individual $r$ and $a$ values. 138

Figure 9.9: Variation of guided resonances with the slab thickness $t$. 139
Figure 9.10: Shift in the positions of resonances as a function of the slab thickness $t$.................................140

Figure 9.11: Same as Figure 9.9, but for a different sample.................................141

Figure 9.12: Electric field distributions at the input facet of the slab, for the three crystals whose transmission spectra are shown in Figure 9.11 ..........142

Figure 9.13: Same as Figure 9.9, but for a different sample.................................143

Figure 9.14: A portion of the relative phase spectrum, for the three crystals whose transmission spectra are shown in Figure 9.13 ..........144

Figure 9.15: Calculated line shape of the lowest-frequency resonance as a function of the slab thickness, for a photonic crystal slab with $r = 150 \, \mu m$, and $a = 400 \, \mu m$ (Figure 9.9). A frequency resolution of 0.1 GHz is used in the FEM simulations.................................145

Figure 9.16: The FEM model for the square lattice photonic crystal.........................147

Figure 9.17: A comparison of the transmission spectra of slabs with identical structural parameters but different lattice structures.........................147

Chapter 10: The effect of structural disorder on guided resonances

Figure 10.1: A schematic of the experimental setup.................................153

Figure 10.2: A top view of the photonic crystal slab.................................154

Figure 10.3: Normal-incidence transmission spectrum of a photonic crystal slab with $r = 150 \, \mu m$, $a = 400 \, \mu m$, and $t = 250 \, \mu m$.................................155

Figure 10.4: Distribution of the hole diameter for perfect and imperfect samples......156

Figure 10.5: Transmission spectra of samples with disorder in the hole size.........157
Figure 10.6: Top-view images of photonic crystal slabs showing disorder in the hole shape.................................................................159

Figure 10.7: Transmission spectra of a sample with disorder in the hole shape........160

Figure 10.8: Top-view images of photonic crystal slabs with disorder in the lattice parameter..............................................................................162

Figure 10.9: Transmission spectra of samples with disorder in the lattice parameter...163

Chapter 11: Summary of results and future directions

Figure 11.1: SEM pictures of the photonic crystal slab waveguides......................169

Figure 11.2: Schematic of a channel drop filter..........................................................170

Figure 11.3: Two-dimensional band structure (TM mode) of a photonic crystal with hexagonal lattice of air holes in silicon........................171

Figure 11.4: FDTD calculation showing electric field distribution in Y-shaped Waveguide, at 0.3 THz.................................................................172

Figure 11.5: Two-dimensional band structure (TM mode) of a photonic crystal with square lattice of air holes in silicon..............................173

Figure 11.6: FDTD calculation showing electric field distribution in 90°-bend Waveguide, at 0.35 THz.................................................................174

Figure 11.7: Images illustrating the design of a channel drop filter.......................175

Figure 11.8: A schematic of the scanning near-field microscopy experiment...........177

Figure 11.9: Electric field distribution measured by the scanning near-field microscope, and the corresponding FEM calculation.................178
Appendix A: Fabrication of THz photonic crystals by photolithography

Figure A.1: A schematic of the mask and wafer design.................................206
Figure A.2: A fabricated 4-inch mask..........................................................207
Figure A.3: Microscopic images of the samples written on the mask..............207
Figure A.4: A schematic of the lithography process.....................................208
Figure A.5: Picture of the mask holder.........................................................210
Figure A.6: Picture of the rear side of the mask holder...............................211
Figure A.7: Typical microscopic images of the sample during various stages of
processing.......................................................................................................213
Figure A.8: Profilometer data obtained from a typical sample......................214

Appendix B: Numerical computation of the superprism effect

Figure B.1: First Brillouin zone of the face-centered-cubic (FCC) lattice..........218
Figure B.2: Plot generated by ds001pnc2.m matlab code ..............................223
Figure B.3: Plot generated by ds001pc2.m matlab code ...............................224
Figure B.4: Plot generated by ds001phd.m matlab code...............................226
Figure B.5: Plot generated by sliced.m matlab code .................................227
LIST OF TABLES

Chapter 6: Colloidal photonic crystals formed by spin-coating

Table 6-1: Measured and ideal lattice parameters of the hexagonal unit cell............89

Chapter 9: Guided resonances in terahertz photonic crystal slabs

Table 9-1: The best fitted values of $\omega_j$ and $\gamma_j$ for the first seven guided resonances in the spectrum shown in Figure 9.2(b).................................130

Table 9-2: Shifts in the positions of first three resonances for a 2% change in the $r/a$ ratio, the hole radius, and the lattice parameter.........................136

Chapter 11: Summary of results and future directions

Table 11-1: Design parameters for THz photonic crystal waveguides in a hexagonal lattice.........................................................172

Table 11-2: Design parameters for THz photonic crystal waveguides in a square lattice.........................................................174

Appendix A: Fabrication of THz photonic crystals by photolithography

Table A-1: Photonic crystal samples for the study of guided resonances ...............204

Table A-2: Various THz photonic crystal waveguide structures...........................204
The semiconductor revolution, which started in the late 1940’s, improved the living conditions in the society in an unprecedented way. These artificial electronic materials, that control the flow of electrons on a microscopic scale, remain an important material in today’s electronics industry. Likewise, the modern photonics industry began in the 1960’s with the invention of laser. This was followed, in the late 1970’s, by the perfection of optical fibers as an effective means of transmitting optical information. When these technologies moved from the laboratory into the application phases in the 1980’s, there was a need for advanced photonic materials to manipulate the flow of light in a more intelligent and efficient way. In 1987, photonic crystals were proposed as optical analogues to electronic semiconductors, having peculiar properties for controlling light propagation at the microscopic scale. This thesis presents theoretical as well as experimental studies on photonic crystals at visible, x-ray, and terahertz frequencies.

Photonic crystals are a new class of materials, allowing control over light propagation at the microscopic level. They consist of dielectric structures arranged in a periodic fashion, due to which the refractive index in these materials is spatially modulated with a period comparable to that of the electromagnetic wavelength. This results in multiple scattering of photons giving rise to photonic band structure, similar to the way electrons are excited in a semiconductor crystal. The band structure may or may not contain gaps (forbidden frequency regions). Both the forbidden and the allowed states can be utilized for specific technological applications through intelligent design and fabrication. While the photonic band gaps prohibit the propagation of light, the allowed
modes can make light of desired frequencies propagate in desired directions. Incorporation of controlled defects in these structures allows for light localization which opens up very interesting applications like inhibition of spontaneous emission. Photonic crystals provide a unique platform to engineer materials and mold the flow of light for novel photonic technologies.

The thesis starts with a detailed introduction on the history of the photonic crystal research, followed by discussions on various applications, and current state-of-the-art in fabrication and simulation methods. Chapter 2 discusses the photonic crystals at different frequency regimes: how the length scale and the material properties in any frequency range affects the photonic crystal characteristics.

Chapters 3 to 6 deal with colloidal photonic crystals that are active in the visible frequency range. In Chapter 3, the theoretical analysis of superprism effect in macroporous polymer photonic crystals is presented. These crystals are fabricated by using colloidal crystals as templates, and their peculiar dispersion property (superprism effect) can be utilized to design a novel chemical sensor (Chapter 4). Chapter 5 describes the experiment that was done to realize the superprism effect presented in Chapter 3. In Chapter 6, fabrication and characterization of colloidal crystals with a non-close-packed lattice is described. This unconventional non-FCC lattice should enhance the functionality of the colloidal photonic crystals and could be useful for applications that require a highly porous lattice.

Chapter 7 describes a three-dimensional photonic crystal at x-ray frequencies. The crystal is obtained from a non-toxic plant virus, the Cowpea Mosaic Virus (CPMV). These crystals have long-range order and represent a sturdy structure with nanometer
scale detail. From an optical point of view, they can be considered as periodic systems capable of manipulating x-ray propagation, since their unit cell dimensions are of the order of nanometers. Calculations predict that metal loaded virus crystals exhibit a normal-incidence reflectivity of 7% for wavelengths around 35 nm, which can be utilized for soft x-ray optical systems.

Chapters 8 to 10 discuss photonic crystal slabs at terahertz (THz) frequencies. They are fabricated using standard lithographic and etching techniques. Experimental and theoretical studies on the superprism effect are presented in Chapter 8. The analyses reveal that the finite thickness of the crystal needs to be considered for accurate prediction of the experimental results. Chapter 9 discusses the variation of guided resonances in THz photonic crystal slabs, as a function of the structural parameters, including the slab thickness. Studies on the effect of structural disorder on guided resonances (Chapter 10) shows that the resonances are very tolerant to disorder in the hole radii but very sensitive to disorder in the lattice periodicity.

The last chapter, Chapter 11, summarizes all the results, and also puts forward suggestions for future work. Waveguide structures and channel drop filters at THz frequencies are proposed. An experiment for studying the near-field Fano resonances in THz photonic crystal slabs is also described. Appendix A explains the standard microfabrication steps for the THz photonic crystal, and Appendix B explains the computer codes that were written to analyze the superprism effect.
Chapter 1

Photonic crystals

Photonic crystals are periodic structures capable of controlling the propagation of electromagnetic waves. By appropriately designing a photonic crystal, one can manipulate the way light propagates inside it [1]. As a result, photonic crystals have been proposed or demonstrated for use as a powerful means to manipulate, confine and control light in one, two or three dimensions of space [2, 3].

This chapter presents a chronological background of the photonic crystal research. After a brief introduction on the concept of photonic crystals, techniques for their fabrication and simulation are discussed.

1.1 Basic concept

Waves in a periodic medium undergo multiple scattering when their wavelengths are comparable to that of the period in the medium. For example, electrons undergo multiple scattering in a crystal from atoms distributed periodically in space. While constructive interference gives rise to allowed electronic states such as valence and conduction bands, destructive interference gives rise to forbidden states. The allowed electronic energies form bands separated by gaps of forbidden energy states or electronic band gaps. By analogy to electrons in crystals, photons – or electromagnetic waves – undergo multiple scattering in a dielectric structure whose index of refraction is spatially modulated with a spatial period comparable to the electromagnetic wavelength.
Periodicity defines dimensionality of photonic crystals, as shown in Figure 1.1. If the index of refraction changes periodically along one direction only, then the material is a one-dimensional (1-D) photonic crystal. Similarly, a two-dimensional (2-D) photonic crystal has refractive index varying periodically along two directions. In some crystal structures with a three-dimensional (3-D) periodicity in refractive index, there are no propagation modes in any direction for a range of frequencies, giving rise to a complete photonic band gap.

![Figure 1.1 Examples of one, two and three-dimensional photonic crystals. The different colors represent different values of refractive indices. Figure taken from Reference [1].](image)

The physical basis of electronic and photonic band gaps is the same, namely the coherent interference of waves scattered from periodically distributed scatterers in space. While electronic band gaps relate to electrons in a crystal, photonic band gaps relate to photons in a periodic dielectric structure. Hence, we find basic similarity in features like Brillouin zones, dispersion relations, complete energy gaps, etcetera. However, there are important differences. First, the wave nature of the electron required for the interference effects depends on a quantum mechanical approach. The electron is treated as a scalar wave with a DeBroglie wavelength. The electronic wave function must satisfy Schrodinger’s scalar equation while the electromagnetic wave function must satisfy
Maxwell's vector equations. The properties of electrons are governed by Schrodinger's equation:

\[
\frac{-\hbar^2}{2m} \nabla^2 \psi(r) = \{E - V(r)\} \psi(r)
\]  

(1.1)

and the properties of photons are governed by Maxwell's equations:

\[
\nabla \cdot D = \rho \\
\nabla \cdot B = 0 \\
\n\nabla \times E = -\frac{\partial B}{\partial t} \\
\n\nabla \times H = \frac{\partial D}{\partial t} + J
\]

(1.2)

Assuming that the medium is isotropic \((D = \varepsilon E)\), and has no free charges or currents, \((\rho = J = 0)\), the above equations become simpler. By further assuming the magnetic permeability to be unity \((B = H)\), and the dielectric function \(\varepsilon(r)\) to be frequency independent and purely real, these equations can be cast in a form similar to the Schrodinger's equation \([1]\):

\[
\nabla \times \left( \frac{1}{\varepsilon(r)} \nabla \times H(r) \right) = \left( \frac{\omega}{c} \right)^2 H(r)
\]

(1.3)

Both Equations (1.1) and (1.3) are linear eigenvalue problems whose solutions are determined entirely by the properties of potential, \(V(r)\), or dielectric function, \(\varepsilon(r)\), respectively. Therefore, if one were to construct a crystal consisting of a periodic array of microscopic uniform dielectric atoms, then, as in the case of electrons, the photons could
be described in terms of a band structure. So, the basic feature of band structure is similar although there is a difference in the equations the electrons and the photons follow. There are more important differences between the electrons and their photonic counterpart. While electrons are fermions, photons are bosons, and electron-electron interactions are strong while there are no photon-photon interactions at any intensities.

Although the word photon is used, the appearance of band gaps arises from a strictly classical treatment of the problem. The propagation (or forbidden state) can be computed from the classical vector wave equation in a material with a periodic index. The principal feature of periodic structures is their ability to perturb the density of electromagnetic states within the structure. It is worthwhile to mention that the propagation of electromagnetic waves in periodic dielectric structures is not a new topic. Devices such as optical gratings, volume holograms and distributed feedback lasers are well known and have been studied extensively. However, the propagation of light in these devices is forbidden only for a small range of wave-vectors and the index contrast is typically of the order of 0.1% of the average index. The creation of a complete photonic band gap requires a large index contrast, typically of the order of 2:1 or greater [4].

1.2 Applications of photonic crystals

By appropriately designing a photonic crystal, one can utilize the allowed and forbidden states of photons and control the propagation of light. The principle feature of photonic crystals is their ability to affect the radiative dynamics within the structure. At the outset, Yablonovitch [5] had suggested that the photonic crystals could change the
properties of the radiation field in such a way that there would be no electromagnetic modes available in the dielectric structure. If the radiative transition frequency of an excited atom was to lie within the band gap then the atom would be incapable of coupling its energy to the surrounding medium due to absence of available modes. The atom would stay in an excited state leading to the inhibition of spontaneous radiative decay. Since spontaneous decay is a major source of energy loss, speed limitation and noise, its suppression could strongly enhance the performance of optical devices such as semiconductor lasers. The same concept can be used in transmitters [6, 7]. For instance, an antenna mounted on a conventional dielectric substrate emits the majority of its radiation into the substrate itself. If the substrate is engineered into the form of a photonic crystal with a gap at the radiation frequency, the losses can be minimized. Other applications include angular filters [8] and cladding material for preventing losses in waveguide structures that contain bends or junctions [9-11]. The performances of such devices have been analyzed at around 1.55 μm [12, 13]. Photonic crystals can also be used in frequency selective mirrors [14], band-pass filters [15], optical resonators [16], and channel-drop filters [17] by creating controlled defects within the periodic lattice.

One of the major thrusts in fabrication has been the realization of photonic crystals for visible and near-infrared frequencies. In this regime, colloidal crystals have been demonstrated as sensors [18] and fingerprinting materials [19]. But the main applications are in the telecommunications, which will require large-scale production of 3-D photonic crystals with gap centered around 1.55 μm [20]. These applications may include the design of zero-threshold micro-lasers [21], light emitting diodes [22] which exhibit good coherence properties, and all-optical transistors [23]. Photonic technology,
using light instead of electrons as a unit of information, paves the way for a new technological revolution in communication and information management systems. A photon has several advantages over an electron. It can travel in a dielectric material at greater speeds than an electron in a metallic wire. Light can also carry a large amount of information per second.

Most of the work in this field has relied on the manipulation of the photonic band gap, or the forbidden states for the photons. A photonic crystal with a full photonic band gap is like a photonic insulator in which photons are not allowed to propagate. However, one can utilize the allowed states for photons and employ photonic crystals as novel photonic conductors. Superprism phenomenon in photonic crystals is an effect that utilizes the allowed states for photons to manipulate the propagation of light [24]. One implication of superprism effect is negative refraction [25], which is very promising for imaging with sub-wavelength resolution, and creation of a superlens [26]. Sensors based on guided resonances in photonic crystal slabs are another example where allowed modes (above the light line) are utilized [27].

1.3 Historical background

A naturally occurring example of a photonic crystal is the gemstone opal, whose opalescence comes from Bragg diffraction of light from the crystal’s lattice planes [28]. Many biological objects, like the wings of a butterfly or the cuticles of a beetle also have periodic structures [29]. However, to have precise control over the optical properties of such structures, one has to build artificial crystals. The first suggestion of a complete gap for electromagnetic waves was made by Yablonovitch [5] and John [30] in 1987.
1.3.1 Development in fabrication and theory

Fabrication of one-dimensional (1-D) and two-dimensional (2-D) photonic crystals has been relatively straightforward. For example, 1-D systems can be easily generated through programmed deposition of alternating layers of different dielectric materials [31], while 2-D systems can be routinely produced via selective etching of the underlying substrates through masks [32]. Fabricating of three-dimensional structures has always been challenging, and the earlier methods relied on self-assembly [33-36] and layer-by-layer approach [37].

The first photonic crystal (called Yablonovite) was fabricated by drilling holes in a dielectric block [38]. It consisted of a dielectric block with a triangular array of holes, each being drilled three times at an angle of 35.26° away from the normal and spread 120° on the azimuth. This led to the first experimental demonstration of a three-dimensional (3-D) photonic crystal. The gap was in the microwave region since the periodicity of the Yablonovite structure was of the order of centimeters.

Theoretical investigations were also being carried out in parallel. Simple analytical conditions for the generation of photonic band gaps had predicted the existence of a gap for an index contrast as low as 1.21 in one case [5] and 1.46 in the other [30]. But these analyses did not take into consideration certain aspects of the problem such as field polarization. The index contrast of 1.21 and 1.46 would then be more appropriately labeled as lower limits.
Initially, a scalar approximation was used [39, 40] to compute the dispersion relations of periodic structures. The vector wave equation was reduced to a scalar equation analogous to Schrodinger’s equation used in electronic band theory. Although the comparison between photons and electrons was attractive, it rapidly became apparent [41] that the scalar theory used for the computation of electronic bands in crystals was inadequate for the computation of photonic band gaps. By neglecting the vector nature of the electromagnetic waves, theoretical results did not agree with the experiments. For example, the existence of large photonic gaps was predicted for face-centered-cubic (FCC) structures of dielectric spheres while none were observed in the experiments [41].

A full vector analysis was then undertaken to solve Maxwell’s equations by taking into account the vector nature of the electromagnetic field [42]. The calculation of dispersion relations for the FCC structure of air spheres in a dielectric background gave symmetry-induced degeneracies. This degeneracy was lifted when diamond structure - an FCC structure with two atoms per Wigner-Seitz unit cell - was used. It then became apparent that the use of any nonspherical basis in the FCC structure would lift the degeneracies. Photonic band gaps were predicted to be as large as 29% of the central frequency for an index contrast of 3.6 in the diamond structure [43]. It was also predicted that the gap should remain open for an index contrast as low as 2.1. Many other structures such as 2-D square and triangular lattice of rods and 3-D simple cubic and body-centered-cubic (BCC) structures were studied [44], and they have been found to yield photonic band gaps. Theoretical calculations have shown that the structure requiring the lowest index contrast to yield an absolute gap is a type of diamond structure requiring an index contrast of 1.87 [43].
In 1992, theorists began to question the accuracy of their numerical results [45]. The computation of photonic dispersion relations had been carried out with the plane wave method, which expanded the electric field and the dielectric function in infinite series of plane waves. The electromagnetic problem was reduced to an infinite-dimensional eigenvalue problem which was solved with standard matrix-diagonalization methods [43]. This required the storage and manipulation of large matrices. While an infinite series expansion of the electric and magnetic fields should have led to the same solutions - since electromagnetic fields are complementary - the truncation of the matrix equation affected the solutions. The number of plane waves used in the expansion was dictated by the available computer time and memory. Another problem associated with the plane-wave method was the poor representation of discontinuous functions [such as \( \varepsilon(r) \)] near the discontinuities. Sozuer et al. [46] used Gaussian functions which provided good convergence of the eigenvalues. To approximate a discontinuous function, Villeneuve and Piche [4, 47] used continuous high-order supergaussian functions and showed that the plane-wave expansion method could lead to reliable and accurate results.

Other numerical methods that do not require the storage and handling of large matrices have been presented for computing photonic band gaps. For example, Johnson et al. [48] have developed a program that computes definite-frequency eigenstates of Maxwell’s equations in periodic dielectric structures for arbitrary wave-vectors, using fully-vectorial and three-dimensional methods. It is especially designed for the study of photonic crystals, but is also applicable to many other problems in optics, such as waveguides and resonator systems. Pendry et al. [49] presented the transfer matrix method (TMM), which allowed them to determine the transmission from finite-sized
slabs of periodic or disordered material without storing large matrices. The TMM calculates transmission coefficient by imposing the Bloch boundary conditions. The absorption effects can also be analyzed as the TMM allows the dielectric constant to be defined as a complex number. These details cannot be studied in the plane wave method. However, sometimes the discretization of the refractive index in TMM is such that dubious results are obtained. This is because the eigenvectors produced are orthogonal to themselves and cannot be normalized [50]. Recently, other techniques have been developed that iterate Maxwell’s equations in time [51]. Maxwell’s equations for both electric and magnetic fields are iterated directly in real time and space using completely general coordinate system. Then time dependent information is Fourier transformed into the frequency domain. Finally, through analyzing of frequency domain information one could obtain a structure of photonic bands as well as transmission and reflection coefficients and spectral characteristics of photonic density of states. This method is based on an extension of the finite-difference time-domain (FDTD) method, originally proposed by Yee [52], also known as the Order-N method [53], which has recently become a popular way of calculating photonic band structures. It is a simple scheme for calculating Green’s functions for photons propagating in complex structured dielectrics.

1.4 Current methods of fabrication

The description of light propagation in photonic crystals involves the solution of Maxwell’s equations with a periodic dielectric function. One of the appealing aspects of Maxwell’s equations is that there is no fundamental length scale. Thus the solutions are scale invariant, which means that if the Yablonovite structure is scaled down to
sufficiently small dimensions (comparable to the wavelength of visible light), a structure is obtained that has a complete band gap in the visible. The most important applications of photonic crystals are in the visible or near-infrared wavelengths. To develop such technologies, like planar waveguides and thresholdless lasers, the fabrication of photonic crystals operational at these wavelengths requires a detailed control over the sub-micron or nanometer length scale. Over the last decade, a variety of fabrication techniques have been developed.

One-dimensional photonic crystals are easily fabricated by alternate deposition of different dielectric materials [31], while two-dimensional crystals are routinely produced via lithographic methods, such as photolithography and electron beam lithography [32, 54, 55]. These lithographic methods are very useful for fabrication of 2-D photonic crystals, but their processing difficulties, however, have so far limited the formation of 3-D structures only up to a number of layers (less than 10) [37, 56]. Around the visible region, one needs to pattern the dielectric materials into microstructures of 100-300 nm in size along all three dimensions, and also accomplish registration among these structures in different layers with an accuracy of better than tens of nanometers. These technical challenges to extending the conventional microlithographic techniques to 3-D patterning have made it necessary to consider some alternative approaches [57]. Promising results have been obtained from layer-by-layer micro-assembly [37, 58, 59], holographic lithography [60, 61], two-photon polymerization [62], and deep x-ray lithography [63]. Three-dimensional photonic crystals with large areas can be manufactured by methods like electrochemical etching [64], auto-cloning [65], glanced-angle deposition [66], and colloidal self-assembly [67-69]. The last technique, colloidal self-assembly (described in
Chapter 2), has emerged as a workhorse for preparing three-dimensional photonic crystals since it can produce large-area colloidal crystals of precisely controlled thickness in a matter of a few days.

1.5 Advanced simulation techniques

To be able to create photonic crystal based optical circuits and devices, their precise electromagnetic modeling is very important. From the viewpoint of electromagnetic field theory, photonic crystals are optical materials with periodic perturbation of macroscopic material constants. During the past decades, various computational techniques and softwares have been developed to formulate the electromagnetic scattering, guiding, and coupling problems in periodic structures. All these methods solve the Maxwell’s equations to characterize light propagation in photonic crystals. The Maxwell’s equations are [Equation (1.2) above]:

\[
\begin{align*}
\nabla \cdot D &= \rho \\
\nabla \cdot B &= 0 \\
\n\nabla \times E &= -\frac{\partial B}{\partial t} \\
\n\nabla \times H &= \frac{\partial D}{\partial t} + J
\end{align*}
\]

Methods that numerically solve these partial differential equations are plane-wave method, transfer matrix method, finite elements method, and the finite-difference time-domain technique. The last paragraph of Section 1.3.1 mentions these methods. Brief descriptions of these methodologies are presented below.
1.5.1 Plane Wave Expansion Method

The plane wave method solves the Maxwell’s equations by reducing them into a linear eigenvalue equation. If there are no light sources present, then there are no free charges or currents in the medium. This means that the charge density, $\rho$, and the current density, $J$, are equal to zero. With these assumptions, the Maxwell’s equations take a much simpler form:

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}$$
$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$
$$\nabla \cdot \mathbf{D} = 0$$
$$\nabla \cdot \mathbf{B} = 0$$

(1.4)

Starting from these equations, we can make some reasonable assumptions. First we assume that the medium is isotropic leading to a scalar relation between $\mathbf{D}(r,\omega)$ and $\mathbf{E}(r,\omega)$. Second, we assume that there is no frequency dependence of the dielectric. In other words, the dielectric function is a constant over the range of frequencies we consider. Third, we assume the material to have negligible loss. This means that $\varepsilon(r)$ is purely real. We also assume that the magnetic permeability is equal to unity. All these assumptions, together with a series of deductions, produce the following equations [1]:

$$\nabla \times \left( \frac{1}{\varepsilon(r)} \nabla \times \mathbf{H}(r) \right) = \left( \frac{\omega}{c} \right)^2 \mathbf{H}(r)$$

(1.5)
$$\nabla \cdot \mathbf{H}(r) = 0$$
The first equation is the master equation. Solution of this linear eigenvalue equation gives the magnetic field. The electric field can then be recovered from the magnetic field.

These equations are solved by expanding \( H(r) \) and \( \epsilon(r) \) into a set of plane waves. As \( \epsilon(r) \) is periodic, \( H(r) \) shares its periodicity. The master equation is converted into a group of linear equations that can be readily solved using a computer. In the plane wave method, only linear equations are solved, therefore the computation time is minimized.

To get accurate solutions, a large number of plane waves must be included in the expansion of \( H(r) \) and \( \epsilon(r) \). Also, the dielectric function \( \epsilon(r) \) should be appropriately discretized. As \( \epsilon(r) \) is not continuous, it introduces significant convergence difficulties. By using proper interpolation schemes and more meshing elements, the error can be minimized.

A widely used plane wave technique is the MIT Photonic-Bands Package (MPB), a freely available software developed by researchers at Massachusetts Institute of Technology [48]. Plane wave methods are limited in their simulation abilities because metallic structures and absorbing materials cannot be analyzed by this technique. Also, finite geometries cannot be analyzed because this method relies on the periodic boundary condition. These limitations can be overcome by using computational techniques like finite-difference time-domain (FDTD), finite elements method (FEM), or the transfer matrix method (TMM), which allow defining exact geometries with appropriate boundary conditions.
1.5.2 Finite-Difference Time-Domain method (FDTD)

The FDTD technique has emerged as an effective tool to computationally model many scientific and engineering problems dealing with electromagnetic wave interactions with materials. It overcomes the limitations of the plane wave method. As it is a time-domain method, solutions can cover a wide frequency range with a single simulation run.

The basic idea of FDTD was introduced by Kane Yee in 1966 [52]. After defining the appropriate geometry in the computational domain, the Maxwell's equations (in partial differential form) are modified to central-difference equations, discretized, and implemented in the software. The equations are then solved in a leapfrog manner: the electric field is solved at a given instant in time, then using the obtained electric field, the magnetic field is solved at the next instant in time, and the process is repeated over and over again. The advantage of this explicit time-stepping scheme is that the need to solve simultaneous equations is eliminated. However, this scheme mandates an upper bound on the time-step to ensure numerical stability. As a result, certain classes of simulations can require many thousands of time-steps for completion, which in turn requires a lot of computer time and memory.

To simulate how electromagnetic waves interact with a material structure, a computational domain containing the structure must be defined, and the source and the boundary conditions must be specified. Finally, the domain is discretized into many smaller subdomains. Depending on the simulation geometry, the FDTD technique can be computationally demanding. There are various university-developed and commercial FDTD softwares available for simulation of photonic crystal structures. A commercial
software that was used to obtain results presented in this thesis is the FullWAVE v3.0.1 from RSoft Design Group [70].

1.5.3 Finite Element Method (FEM)

Finite element method is a numerical technique widely used in analyzing engineering problems that require solutions of partial differential equations. Working separately, Richard Courant [71] and Alexander Hrennikoff [72] developed this method in the 1940s, for analyzing civil engineering and aeronautical engineering problems. Even though the FEM is mostly known for heat transfer and fluid dynamics analysis, it has been generalized into a branch of applied mathematics for numerical modeling of physical systems in a wide variety of engineering disciplines, including electromagnetics.

While the approaches used by the two pioneers were different, they shared the same essential characteristic: defining the geometry (to be analyzed) in a computational domain, and then discretizing the continuous domain into a set of discrete subdomains, that is, finite elements. The accuracy of the FEM is closely related to the quality of discretization. By refining the mesh, the solutions can be made numerically stable, improving the accuracy. For example, accurate simulation of photonic crystals requires a mesh size of less than λ/10, where λ is the wavelength of the electromagnetic wave and depends on the refractive index of the medium. Although this technique requires a lot of computational load (in terms of time and memory), the most attractive feature of the FEM is its ability to handle complex geometries (and boundaries) with relative ease. A commercially available software that utilizes the finite elements technique for numerical
modeling of photonic crystals is the Electromagnetics Module of Comsol Multiphysics [73]. This software was used to generate results presented in this thesis.

Since a set of partial differential equations for a given geometry can be solved in a variety of ways, the choice of appropriate solver to get a stable solution is very important. A variety of solvers are always being developed to minimize the computational time without affecting the accuracy of the solutions.

1.5.4 Transfer matrix method

The transfer matrix method for modeling the optical response of photonic crystals was developed by Pendry et al. in 1992 [49]. This technique can consider a finite thickness of the crystal along the direction of beam propagation, and can incorporate absorption effects by assigning complex dielectric constant values as a function of frequency. It is generally used for calculation of the reflection coefficient (or the transmission coefficient) from a photonic crystal of finite thickness.

Just like the FDTD and the FEM techniques, the transfer matrix method also requires appropriate discretization of the defined geometry. The basic approach in transfer matrix method (TMM) is to compute the fields in a plane, given the respective fields in the previous plane. For example, if the electric and magnetic fields in the $x$-$y$ plane at $z=0$ are known, then Maxwell's equations can be used to integrate the wave-field and calculate the electric and magnetic fields in the $x$-$y$ plane at $z=c$. Basically, using the material properties, the TMM uses a matrix form to express the relationship between fields in adjacent planes. This matrix is called the transfer matrix, $T$:

$$
\mathbf{F} (z = c) = T (c, 0) \cdot \mathbf{F} (z = 0)
$$

(1.6)
By imposing the Bloch boundary condition for the periodic lattice:

\[ F(z = c) = \exp(ikc) \cdot F(z = 0) \]  

(1.7)

and comparing the last two equations, it is evident that the eigenvalues of the transfer matrix will give the wave vector, \( k \), for a particular value of frequency, \( \omega \). By diagonalizing the real space transfer matrix, the wave vectors can be calculated for a range of frequencies, giving the dispersion relation for the infinite crystal. Also, reflectivity from a finite sample can be calculated by transforming the transfer matrix to a plane wave basis.

Although easy to use, this particular transfer matrix technique suffers from some ambiguous problems. For example, if the number of grids used to discretize the geometry is a multiple of 4, then the results obtained are inaccurate because of improper choice of plane waves [50]. Based on a better version of the method developed by Pendry and co-workers, a freely available software, TransLight, was developed by researchers at the University of Glasgow [74].

1.5.5 Applicability of the simulation techniques to photonic crystals

The description of light propagation in photonic crystals involves the solution of Maxwell's equations. One of the appealing aspects of Maxwell's equations is that there is no fundamental length scale. Thus the solutions are scale invariant, which means that if the length scale of any photonic crystal structure is changed, the same properties are observed at a different wavelength. For example, if the Yablonovite structure, which has a complete band gap at microwave frequencies, is scaled down to sufficiently small
dimensions comparable to the wavelength of visible light, the structure will exhibit a complete band gap at visible frequencies. The material properties, however, do not remain the same at different frequency regimes, requiring appropriate choice of the simulation technique.

The same material can have different optical properties in different regions of the electromagnetic spectrum. For example, high-resistivity silicon is transparent at terahertz frequencies, whereas it is an absorbing material in the region around visible and near infra-red frequencies. On the other hand, silica is transparent at visible and near-infrared frequencies, but lossy in the terahertz region. Metals are nearly perfect reflectors at terahertz and microwave frequencies, but they interact readily with visible frequencies, where their plasmon resonances lie. For the x-ray regime, almost every material absorbs, and their complex refractive indices are frequency dependent quantities with the real part close to unity. Because of these differences in material properties at different frequency regimes, the right choice of the simulation method is necessary for obtaining accurate results.

The plane-wave method is commonly used to calculate the dispersion relation of an infinite photonic crystal. But it cannot accurately calculate the dispersion relation for finite crystals, or for structures comprising metals and absorbing materials. In that case, although difficult to implement, the FDTD method can be used to calculate the band structure. In photonic crystal research, it is fairly common to calculate the dispersion relation as the first step. This provides information on band gaps, complete or partial. Almost all photonic crystals possess partial band gaps, and the dispersion relation reveals the crystal planes that will produce high reflectivity to sustain a strong partial band gap.
After that, other techniques like the transfer matrix method can be used to calculate the reflection coefficient of those planes. If an exact geometry needs to be simulated, then the FEM and the FDTD methods are very useful. Although computationally cumbersome, these methods allow exact description of geometry, boundaries, and material properties.

The next chapter presents more details about fabrication and characterization of photonic crystals in different regions of the electromagnetic spectrum.
Chapter 2

Photonic crystals for different frequency regimes

This chapter describes the fabrication and characterization techniques for photonic crystals at different frequency regimes: terahertz, visible, and x-ray. While fabrication of terahertz photonic crystals is very straightforward, that for the x-ray photonic crystals is extremely difficult. The major thrust in fabrication has been the realization of photonic crystals for visible and near-infrared frequencies, because of potential applications in all-optical devices and telecommunications.

2.1 Introduction

In photonic crystals, the scale of periodicity in the refractive index determines the frequency (or wavelength) of the electromagnetic waves that can be manipulated, and is of the same order as the wavelength of the radiation. This means that photonic crystals operating at large wavelengths have relatively bigger features as compared to the photonic crystals that are designed to operate at smaller wavelengths. The electromagnetic spectrum in Figure 2.1 shows the frequencies of different regimes, and their corresponding free-space wavelengths. As the frequency of the radiation increases, the corresponding wavelength decreases. While photonic crystals operating in the radio, microwave, and terahertz regions are easy to develop, fabrication of those active in the visible, ultra-violet, and x-ray regions face difficulties due to smaller wavelengths involved.
2.2 Terahertz photonic crystals

The terahertz (THz) regime exists between the infrared and the microwave regions. THz waves have frequencies between 0.1 and 10 THz. Because of the difficulties involved in making suitably compact terahertz sources and detectors in this region, it is considered as one of the last unexplored regions of the electromagnetic spectrum [75, 76]. With the progress in THz technology [77], various applications in imaging [78-80] and sensing [81] have been proposed. The development of photonic crystals at THz frequencies promises to bring about further advancement by allowing the realization of devices like waveguides, switches, and filters.
The wavelength of the THz waves range from several hundred micrometers to a few millimeters. Therefore, fabrication of THz photonic crystals requires sub-millimeter patterning, which can be easily done by using semiconductor microfabrication techniques. Lithography, micro-machining, dicing, and etching are readily employed to fabricate THz photonic crystals. Figure 2.2(a) shows a three-dimensional woodpile photonic crystal made by micro-machining and wet etching [82], whereas Figure 2.2(b) shows a two-dimensional photonic crystal fabricated by deep reactive-ion-etching [83]. Due to large feature sizes and established fabrication technology, THz photonic crystal can be fabricated with essentially zero structural disorder. Ease of fabricating perfect optical components has also made the THz regime very desirable for analyzing various metamaterial structures [84]. A detailed description of how THz photonic crystal slabs are fabricated by standard lithographic techniques is presented in Appendix A.

![Figure 2.2](image)

Figure 2.2 (a) Three-dimensional woodpile photonic crystal fabricated by micro-machining and wet etching [82]. The silicon rods are 50 μm wide and are placed 180 μm apart from each other. (b) Two-dimensional photonic crystal fabricated by deep reactive ion etching of silicon [83].

To create THz photonic crystals of desired functionality, low-loss materials are required. Because high-resistivity silicon is transparent to THz waves [85] and is
perfectly compatible with established microfabrication techniques, it has been the material of choice. There are also various examples of THz photonic crystals made from metals [86-88], ceramics [89] and plastics [90, 91]. The woodpile structure is the most promising three-dimensional photonic crystal [92], and has been the focus of several recent studies [93, 94]. Three-dimensional THz photonic crystals have also been fabricated using spherical particles [95], and those made from superconductors have been envisioned [96]. In this thesis, THz photonic crystal slabs made from high-resistivity silicon are studied (Chapters 8, 9, 10).

Terahertz time-domain spectroscopy (THz-TDS) is the standard characterization technique that is used for studying the properties of materials in the THz regime. A schematic of this method is shown in Figure 2.3 [97]. The initial laser beam from the femtosecond laser is split into two parts: pump beam and the probe beam. The pump beam hits the transmitter, which in response to the optical pulse releases subpicosecond pulse of THz radiation. The probe beam, after going through an optical delay line, gates the detector. The response of the detector is proportional to the amplitude and sign of the electric field of the THz pulse that it receives. By varying the delay between the pump and the probe beams, the whole profile of the THz pulse can be traced. The complex transmittance of a sample is given as the ratio of the Fourier transforms of a pulse transmitted through the sample and a reference, usually the freely propagating pulse.

The transmitter emits THz radiation through a photoconductive switching method. The optoelectronic switch (called Auston switch [98]) consists of two 5 μm wide, 5 μm thick gold electrodes separated by about 10 μm. The electrodes lie on a semiconductor substrate, typically a semi-insulating GaAs wafer. A DC bias of tens of voltages across
the two gold lines creates a strong electric field. The femtosecond laser pulses (Ti:sapphire, central wavelength 800 nm, pulse length 100 fs, average mode-locked power 390 mW), when focused onto the transmitter, excite photocarriers in the substrate, and a transient photocurrent is produced under the influence of the strong DC field. The current rises rapidly and then decays with a time constant given by the lifetime of the semiconductor substrate, and in the process short pulses of electromagnetic waves in the terahertz regime are transmitted. The emitted THz radiation is focused by lenses made of high-resistivity silicon or teflon, since these materials are transparent to the THz waves. The detector is a low-temperature-grown GaAs, which has a shorter carrier lifetime than the THz pulse duration, and is essential for accurate measurements. To obtain a high signal-to-noise ratio, a lock-in amplifier (Princeton Applied Research, Model 124) is used in the experiments. Commercial THz-TDS systems, like T-Ray 2000 from Picometrix, Inc., combine the optics into one black box. These systems are very convenient to use since the transmitter and detector are fiber-coupled, allowing for their easy movements, which provide flexibility in experimental setups.

![Figure 2.3 Schematic of THz-TDS. Taken from Reference [97].](image-url)
2.3 Photonic crystals at visible frequencies

Because of the promise of all-optical devices, fabrication of photonic crystals at visible frequencies has always been desirable. Electromagnetic waves in the visible regime have wavelengths between 300 nm and 800 nm. Therefore, for photonic crystals to operate at visible frequencies, their feature sizes should be in the sub-micron range. Self-assembly methods using colloidal microspheres provide an easy route for fabrication of three-dimensional photonic crystals in the visible range [99]. Lithographic methods are more useful for two-dimensional structures only. This is because scaling down the features to sub-micron limits using lithographic techniques is expensive and cumbersome [37].

Various techniques have been used to fabricate photonic crystals at visible frequencies: holographic lithography [60], two-photon polymerization [61], spin-coating [100, 101], and colloidal self-assembly [33, 68, 69, 102]. With the exception of colloidal assembly methods, all the other techniques require advanced instrumentation and are expensive to maintain. The two colloidal techniques that are most widely used are gravity sedimentation [33] and controlled drying [68]. The latter has emerged as a workhorse for preparing three-dimensional photonic crystals since it can produce large-area colloidal crystals of precisely controlled thickness in a matter of a few days. Opal-based colloidal crystals have been demonstrated for a variety of applications, from mirrors and filters [103], to waveguides [104], sensors [18] and fingerprinting materials [19]. They have also been used as templates for fabrication of various photonic structures and devices [105-110]. As the telecommunication wavelength of 1.55 μm in the near-infrared, not far
from the red side of the visible spectrum, a colloidal crystal was used to create an inverted-opal silicon structure with a band gap at around 1.5 μm [20]. The next section describes the convective self-assembly method for the fabrication of opal-based photonic crystals.

2.3.1 Colloidal crystals: fabrication

Colloidal crystals are regular crystalline arrays of highly monodisperse microspheres of dielectric materials such as silica or polymers. These crystals have attracted the attention of physicists for several decades. For example, mineralogical and X-ray studies revealed that precious gemstone opal is a hydrated amorphous form of silica – the most common material on Earth [28]. The iridescent colors of the natural opals are due to the Bragg diffraction of visible light by highly ordered sub-micron silica microspheres, as seen in Figure 2.4.

Figure 2.4 Naturally occurring gemstone opal consists of domains of ordered silica microspheres. These randomly oriented domains diffract different wavelengths of light in different directions, giving opal its iridescence. A scanning electron microscopic image on the right reveals the microscopic order produced by natural self-assembly [28].
Self-assembly offers an effective route for fabrication of three-dimensional structures. In this process, pre-designed building blocks spontaneously organize themselves into a relatively stable structure through non-covalent interactions. The inherently parallel nature of the self-assembly process makes this approach well suited for a large-scale production process where low cost and high output are the two key requirements. The natural self-assembly process of opal formation has been mimicked in the laboratory to produce single domain synthetic opals that are ordered on a much larger scale. The most used techniques are gravity sedimentation [33], physical confinement [111], sonication [112], and convective self-assembly [68].

The silica microspheres are the starting materials from which synthetic opals are fabricated. The quality of colloidal crystals depends on the monodispersity of the starting particles. Therefore, the first requirement in order to build technologically interesting materials is to control the production of well-shaped size-controlled spherical silica particles. The most common method is that developed by Stober et al. [113]. It consists of a sol-gel process in which a Si-alkoxide compound is hydrolyzed creating Si-O chains, which condense to form amorphous silica nanoparticles. Under controlled reaction conditions, monodisperse spheres (less than 5% in dispersion) with diameters in the range of 200-700 nm can be produced.

Gravity sedimentation is one of the earliest techniques for fabrication of synthetic opals [33, 35, 67, 114]. In this method the colloids are suspended in a liquid at a critical volume fraction. Under vibration free conditions the colloids sediment due to gravitational forces, to the bottom of a vial where they arrange themselves into a face-
centered-cubic (FCC) lattice. Films prepared in this manner have many polycrystalline domains, each approximately one square millimeter in area. The crystal formation occurs only at specific volume fractions of the colloidal solution, so it is difficult to control the crystal growth. As a result the film thickness is not adjustable. This method provides very thick films but takes about a month to grow a single sample. A faster method called convective self-assembly is more useful for the fabrication of opals in a controlled manner.

![Figure 2.5](image)

Figure 2.5 Schematic of convective self-assembly. The surface tension of the meniscus draw the spheres towards each other resulting in their being tightly packed. With evaporation, the spheres are deposited uniformly onto the glass substrate.

The convective self-assembly method relies on strong capillary forces to self-organize the colloids into a regular FCC crystal [68]. The arrays are ordered over large areas (~1 cm²) with minimal grain boundaries. The most important feature of this method is that the thickness of the film can be controlled by varying the volume fraction of the colloidal solution. The crystallization process only takes a few days, making it much faster than the sedimentation technique. Figure 2.5 shows the schematic of the process. The photonic crystal is formed on a glass slide immersed in a colloidal solution. The
capillary force of the meniscus draws the spheres towards each other causing them to pack together. As the solution evaporates and the meniscus drops, the lower regions of the glass surface are continuously coated. The thickness of the film can be controlled by adjusting the concentration (or the volume fraction) of the colloidal solution. A higher colloidal concentration results in thicker colloidal crystals, as seen in Figure 2.6.

The silica colloidal crystals are characterized by scanning electron microscopy (SEM). The SEM provides details about the crystal lattice, revealing packing of the spheres and arrangement of the crystal planes along different orientations. Another method of characterization is optical spectroscopy, which is used for studying the optical properties of the crystals. Commercial spectrometers (like Cary UV-Vis 5000) are generally used, although there are examples of custom-made setups for certain special types of analyses (like single-domain spectroscopy) [115, 116].

![Figure 2.6 Cross-sectional SEM pictures showing that a higher colloidal concentration results in a thicker colloidal crystal. Fifty layers are obtained when the volume fraction (V.F.) of the spheres is 3%, whereas a V.F. of 0.8% results in a 13 layer thick sample. Taken from Reference [68].](image)

The silica colloidal crystals provide an ideal scaffold for the creation of both polymeric and inorganic samples with complex porous structures. Such samples may exhibit more complete photonic band gaps than silica-air crystals, as higher index
contrasts are possible. Examples range from inverted opals [20, 69, 105] and photonic superlattices [108, 109] to hollow spheres [106] and waveguides [104]. Several new fabrication methods have also been developed in which the silica microspheres are arranged in a non-FCC lattice, or in a non-close-packed lattice, or both [101, 117, 118].

2.3.2 Colloidal crystals: properties

The colloidal crystals formed by convective self-assembly have face-centered-cubic (FCC) lattice structure, with the \( \{111\} \) plane forming the crystal surface. The dispersion characteristics (or the band structure) of these crystals can be modified by simply altering the size of the spheres. Figure 2.7 shows normal incident optical spectra along the \( (111) \) direction of the crystal lattice. Films with larger spheres exhibit transmission peaks at longer wavelengths. Therefore, the transmission peak can be tuned by varying the sphere diameter.

Although a three-dimensional band structure calculated using the plane wave method predicts the position of the band gap accurately, a simple scalar effective medium theory can also be used for these opal-based crystals [119]. This simple theory assumes that the photonic crystal behaves like a homogeneous diffracting medium with an effective weighted refractive index and that the scattering occurs mainly from the \( \{111\} \) set of lattice planes. If \( \lambda_{\text{gap}} \) is the central wavelength of the gap, \( n_{\text{eff}} \) the effective refractive index of the colloidal crystal, and \( d_{111} \) the spacing between the \( \{111\} \) lattice planes, then according to the simple scalar theory:

\[
\lambda_{\text{gap}} = 2 \times n_{\text{eff}} \times d_{111}
\]  \hspace{1cm} (2.1)
The effective refractive index is given by:

\[
n_{\text{eff}} = \sqrt{\varepsilon_{\text{sphere}} \phi + \varepsilon_{\text{void}} (1 - \phi)}
\]  

(2.2)

where \( \varepsilon \) is the dielectric constant. For a FCC crystal, \( \phi = 0.74 \), and \( d_{111} = \left(\frac{\sqrt{2}}{3}\right)d \), where \( d \) is the sphere diameter. Equation (2.1) is the usual form for Bragg diffraction at normal incidence. Thus, by choosing spheres of a particular refractive index and diameter, the band gap can be obtained at a desired wavelength. For example, in case of silica colloidal crystals (\( \varepsilon_{\text{sphere}} = 1.9044 \), \( \varepsilon_{\text{void}} = 1.0 \)) fabricated from spheres of diameter 279 nm, Equation (2.1) predicts the center-wavelength of the gap at 589 nm, as observed (Figure 2.7).

![Figure 2.7](image)

**Figure 2.7** Normal incidence transmission spectra of colloidal crystals with different sphere diameters. For samples with larger spheres the mid-gap peak shifts to longer wavelengths. Taken from Reference [68].
The band gap can also be controlled by the thickness of the film. Just like in x-ray diffraction theory, thin films with a few layers have broader peaks in transmission spectra than thicker films [120]. As the thickness of the film increases, the peak narrows. This is clearly seen in Figure 2.8, which shows transmission spectra of silica colloidal crystals of different thicknesses. The full width at half maximum (FWHM) narrows as the number of layers in the sample increases. The narrowing of the bandwidth saturates after about 15-20 layers, identical to the dynamical diffraction theory of x-rays [120].

![Figure 2.8 Normal incidence transmission spectra of three samples with increasing film thickness (average sphere diameter = 279 nm). The peak height has been normalized. The thin 7 layer sample has a broad mid-gap peak. As the thickness is increased the peak becomes narrower and saturates beyond 20 layers. The change in thickness can also be seen in the Fabry-Perot fringes (arrows) becoming more closely spaced. Taken from Reference [68].](image-url)
2.4 Photonic crystals at x-ray frequencies

Electromagnetic waves with wavelengths between 1 nm and 50 nm are referred to as extreme ultra-violet or soft x-rays. X-rays have very short wavelengths, generally of the order of a few angstroms. For a photonic crystal to be active in the x-ray region, its feature size has to be of the order of angstroms. By using magnetron sputtering or vapor deposition techniques to lay down alternating stacks of dielectric materials, one-dimensional multilayer films can be easily fabricated [121, 122]. But fabrication of two- or three-dimensional photonic crystals is extremely difficult because of such small wavelengths of x-rays. The fact that refractive indices of materials are complex frequency dependent quantities in this region makes the designing and fabrication processes even more challenging. Equally problematic is the lack of theoretical treatments for these structures. Existing approaches to one-dimensional x-ray optics cannot be transferred to more complex multi-dimensional architectures. Consequently, the widespread use of two- and three-dimensionally patterned materials for x-ray optical elements has been limited.

There are only two examples of three-dimensional photonic crystals at x-ray frequencies. One is the superlattices of voids and gas bubbles in metals, which are formed when certain metals are implanted with inert gas ions, charged particles, or neutrons [123-126]. These gas-bubble superlattices have been proposed as candidates for soft x-ray optical components [127]. Another example is a metallized virus crystal with periodicity around 30 nanometers [128, 129]. These virus crystals promise utility in mirrors and dispersive elements on synchrotron radiation beamlines [130]. They are discussed in more detail in Chapter 7.
The subsequent chapters present the fabrication, characterization, and analysis of photonic crystals at the visible, x-ray, and terahertz frequencies.
Chapter 3

Superprism effect in macroporous polymer photonic crystals

This chapter presents a detailed analysis of superprism effect in three-dimensional macroporous polymer photonic crystals fabricated from colloidal crystal templates. The superprism phenomenon is the extremely large angular dispersion experienced by a light beam when entering a photonic crystal. This arises from the anisotropy of the photonic band structure. Strong anisotropy can be present even in systems without a complete photonic band gap. We explore the extreme sensitivity of the propagation direction to various input parameters, including the input angle, the light frequency, and the composition of the photonic lattice. Such effects can be exploited for sensing and filtering applications.

A part of this chapter is published in Reference [131].

3.1 Introduction

Initially, the study of photonic crystals was motivated by the possibility to study the inhibition of spontaneous emission [5] and the localization of light [30] through the action of complete gaps. Subsequently, most of the work in the field has relied on the control of light propagation through the manipulation of the gaps within the photonic density of states. As a result, the construction of a photonic crystal possessing a full band gap has been a primary goal of the field [20]. However, recently another method has been demonstrated for controlling the propagation of radiation inside a photonic crystal, involving the manipulation of the anisotropy of the bands [24, 132, 133]. Due to this
anisotropy, the propagation direction of light inside a photonic crystal can be an extremely sensitive function of parameters such as the wavelength or the incident angle. This effect, known as the superprism phenomenon, is observed at high frequencies, where anisotropy in photonic band structure is strongest and effects like negative refraction and birefringence are expected [134].

Various theoretical predictions and experimental studies have been reported regarding anomalous angular deviation of light at high frequencies near the photonic band gap. Lin et al [135] reported beam deviation inside a 2-D crystal and attributed the deflection to non-linearity in the dispersion relation near the Brillouin zone edges. Subsequently, it has been realized that the anisotropy of the photonic bands plays a crucial role [24, 136]. The propagation through photonic crystal prisms has been analyzed [132, 137], and a number of applications proposed [133, 138]. This phenomenon has been studied using a transfer matrix approach, in both one and two dimensional crystals [139, 140]. Other theoretical predictions involving the superprism effect have simulated auto-cloned 3-D photonic crystals [24, 65, 141]. Ochiai and Sánchez-Dehesa [142] have extended the discussion to the case of three-dimensional crystals, such as self-assembled colloidal crystals.

In this work, we describe the computation of superprism effect in a macroporous polymer photonic crystal formed from a colloidal crystal template [143]. Following the method outlined by Kosaka et al. for two-dimensional photonic lattices [132], we directly compute the iso-energy surface based on the full three-dimensional photonic band structure, and then determine the propagation angles from the gradient of this surface. Our simulations confirm a very sensitive dependence of the output angle on the
parameters of the incoming beam. In particular, our calculations show a wavelength sensitivity of 14 degrees/nm for an input wavelength of around 1300 nm, substantially larger than the 0.5°/nm dispersion reported for planar photonic crystals [138]. Calculations at constant wavelength show a change of 8 degrees in the internal propagation angle for 1 degree change in the input angle. These sensitivities increase at lower wavelengths. The results substantiate the existence of superprism effect in three-dimensional photonic crystals, and emphasize the potential value of templated colloidal materials. Our technique is quite distinct from the method of Reference [142], in which the analysis relies on the computation of a surface Brillouin zone rather than the complete dispersion surface. As a result, it is not readily generalizable to arbitrary crystal orientations. In addition to a plane wave expansion for calculation of the group velocity, this work also included an analysis of the coupling efficiency across the air-photonic crystal interface, based on a layer-KKR method. This is required because the analysis is done for higher frequencies where many bands can couple. In contrast, we have not considered the issue of coupling, because at lower energies (such as considered here), it is not possible for more than a few bands to play a role. Finally, the technique described here only requires the numerical computation of the band structure, which can be performed to essentially arbitrary precision using available software [48].

Next few sections describe the results obtained by numerical methods. A series of codes were written in Scheme and Matlab, and a tutorial on how to use them is presented in Appendix B. These codes explain the calculation methods for the complete photonic band structure, equal-energy surfaces, internal propagation directions, and various other results.
3.2 Complete photonic band structure

The basis for the superprism phenomena is anisotropy in the photonic band structure, a feature which is strongly present at frequencies near the photonic band gap. The effect is very sensitive to the particular choice of incident angle relative to the orientation of the photonic crystal, as well as the incident wavelength. Hence, accurate theoretical modeling is needed in order to design and orient samples for optimized sensitivity at a given wavelength. Here, we apply our calculation to a particular crystal morphology, namely a macroporous polymer, which is robust and easy to fabricate [105]. These three-dimensional polymer photonic crystals are formed by using colloidal crystals as templates. Macroporous polymer templates can be prepared from high quality silica colloidal crystals with controlled thickness [68]. These are inverted face-centered cubic (FCC) structures, i.e. interconnected air spheres in a close-packed FCC configuration in a polymer background [105]. Though these inverted structures do not provide a high enough dielectric contrast for the formation of a full band gap, they do possess substantial stop bands indicative of a partial gap along the \{111\} crystalline axis [144]. This is an indication of strong band structure anisotropy, which is sufficient for the manifestation of the superprism effect.

The band structure for the macroporous polymer is calculated using an available software package [48] which utilizes the plane wave method. This software computes definite-frequency eigenstates of Maxwell's equations in periodic dielectric structures for arbitrary wave vectors, using fully-vectorial and three-dimensional methods, and is specifically designed for the study of photonic crystals. For better convergence, a grid of $16 \times 16 \times 16$ is taken with mesh size of 7. To simulate the structure of macroporous
polymer templates, we define the lattice geometry for the FCC lattice and set the ratio of sphere radius to the primitive unit cell length to be slightly more than 0.5, \( r/a = 0.53 \). This corresponds to placing the air spheres slightly closer together than their diameters, leading to small windows which interconnect the internal air network [106]. This accurately reproduces the morphology of the samples [105]. The dielectric constant of the polymer background is taken as 2.5281 (corresponding to \( n_p = 1.59 \)), which is roughly the value for polystyrene [145]. The typical band structure for the lowest eight bands is shown in Figure 3.1. Here, \( \Omega \) is the normalized frequency given by \((\omega a/2\pi c)\) or \( (a/\lambda) \), where \( a \) is the length of the primitive unit cell. The inset shows various high symmetry points for the Brillouin zone of an FCC lattice.

The band structure shown in Figure 3.1 is depicted in a standard way for the FCC lattice. It only displays the energy along lines connecting the high symmetry points on the Brillouin zone surface. However, a complete photonic band structure is needed to calculate the dispersion surface. In other words, we must calculate the band structure from the \( \Gamma \) point to all possible points on the Brillouin zone surface, not merely to the high symmetry points. We can of course use the symmetry of the Brillouin zone to reduce the computational load.

3.3 Dispersion surface and propagation direction

The complete photonic band structure gives information about how the band structure varies from \( \Gamma \) point to all possible points on the Brillouin zone surface. From this, all possible values of wave vectors in the three-dimensional space for a particular energy or frequency can be calculated. The plot of all these wave vectors in the \( k \)-space
for a particular energy gives an equal-energy surface known as a dispersion surface. It is analogous to the index ellipsoid in conventional crystal optics or to the Fermi surface in electronic crystals.

![Graph showing dispersive bands in a photonic crystal lattice](image)

**Figure 3.1** Lowest eight bands in the band structure of the inverted FCC photonic crystal lattice, computed using the plane wave method. The dielectric matrix has a refractive index of 1.59 (similar to polystyrene), and the air spheres overlap slightly \((r/a=0.53)\) in order to model an experimentally realizable sample. The horizontal dashed lines represent the energies used to compute the dispersion surfaces shown in Figure 3.3. The inset shows the first Brillouin zone of the FCC lattice, with various high symmetry points labeled.

The shape of the dispersion surface depends on the chosen value of energy, specified by the frequency of the incident light. For small values far below the stop band, the band structure is isotropic in nature. In this case the dispersion surface is spherical, with a radius given by the magnitude of wave vector which corresponds to a velocity of \(c/n_{ave}\), where \(n_{ave}\) is the average (homogenized) refractive index. At high frequency
values, near the photonic band gap, the band structure anisotropy is strong. As a result, the shape of dispersion surface deviates from spherical, though it retains the symmetry of the Brillouin zone.

To understand how this distortion of the dispersion surface leads to the superprism phenomenon, we first examine the band structure at small frequency values. Figure 3.2(a) shows the band structure for the second band at small frequency values, from the $\Gamma$ point to five other high symmetry points on the Brillouin zone surface. At these values of frequency, the magnitude of wave vector for all five directions is nearly the same. As a result, the dispersion surfaces at these energies are spheres in k-space. In contrast, Figure 3.2(b) shows the band structure for the fourth band at higher frequencies. In this case there is a strong dependence of $|k|$ on the direction in k-space. So at higher frequency values, a plot of the dispersion surface in k-space does not produce a sphere, but a distorted shape. The differences in the magnitudes of wave vectors in different directions for a particular value of frequency are essentially the band structure anisotropy.

![Diagram](image)

**Figure 3.2** Band structure from $\Gamma$ point to five different high symmetry points on the Brillouin zone surface, plotted as the energy versus the magnitude of the dimensionless wave vector, $|ka|$. (a) shows the nearly isotropic second band, while (b) shows the anisotropic fourth band. The horizontal dashed lines represent the energies used to compute the dispersion surfaces shown in Figure 3.3.
In Figure 3.3, examples of iso-energy surfaces are shown for the macroporous polymer sample under consideration, at the three energies denoted by horizontal dashed lines in Figure 3.1. We note that these dispersion surfaces retain the symmetry of the Brillouin zone.

Figure 3.3  Iso-energy (dispersion) surfaces computed from the full three-dimensional photonic band structure, a small portion of which is shown in Figures 3.1 and 3.2. (a) Band #2, $\Omega = 0.50$, (b) Band #3, $\Omega = 0.80$, (c) Band #4, $\Omega = 0.73$.

The propagation direction can be obtained directly from the dispersion surface [24, 132]. First, the incident wave vector is obtained by drawing the free space dispersion surface (a sphere), and then drawing a ray from $\Gamma$ point to a point on this surface to represent the incident wave vector $k_{\text{in}}$. The orientation of this incident wave vector defines the incident angles ($\theta_{\text{in}}$ and $\phi_{\text{in}}$). The propagation wave vector inside the crystal is obtained by noting that the component of the wave vector parallel to the crystal surface is conserved across the boundary. Hence, a corresponding point $k_p$ on the photonic crystal dispersion surface is obtained, representing the propagation wave vector for the radiation inside the crystal. Finally, the propagation direction is obtained as normal to the dispersion surface at the end point of the propagation wave vector $k_p$, since the group velocity $v_g$ is given by $v_g = \nabla_k \omega(k)$. If the dispersion surface is spherical, then
this gradient points radially, and the wave propagates in a direction parallel to its wave vector. As a result, the propagation angle does not change drastically for small changes in the incident orientation. However, if the dispersion surface is distorted, then the gradient can be a sensitive function of the incident angle. Sensitivity in wavelength arises from the fact that the shape of dispersion surface changes with small change in frequency. The more distorted the shape of the dispersion surface, the more drastic is the change in propagation direction and hence the more pronounced is the superprism effect.

We note that this analysis neglects the parity of the bands, which influences the coupling efficiency from free space into the photonic crystal modes, depending on the incident light polarization [142]. However, since in a three-dimensional lattice the modes are not pure TE or TM, both s- and p-polarized light exhibit some degree of coupling. We expect that p-polarized light couples more efficiently for the specific orientations described here because the modes have odd parity (with respect to the \{110\} symmetry plane in which the internal propagating k-vector is confined). In any event, the incident polarization is not relevant in computing the variation of the internal propagation angle with incident angle or wavelength, since the propagation direction is determined entirely by the shape of the dispersion surface.

3.4 Results and discussion

With the computed dispersion surface, it is possible to calculate the incident and propagation angles with respect to any set of planes in the crystal, or equivalently for any arbitrary crystal orientation or facet. For illustrative purposes, we calculate here the results with respect to the \{111\} set of planes since they are most readily accessible
experimentally [68, 105]. We also report a few results for the \{001\} face since it is possible to grow the colloidal crystals with this face exposed by employing specially patterned surfaces [146, 147].

As we are dealing with three-dimensional crystals, the orientation of the incoming beam is defined by two parameters, \(\theta_{\text{in}}\) and \(\phi_{\text{in}}\). Similarly, \(\theta_{p}\) and \(\phi_{p}\) define the internal propagation direction. The dispersion surfaces obtained at different frequencies differ in shape but retain the symmetry of the Brillouin zone. It is clear from Figure 3.3 that the gradients of these dispersion surfaces will not, in general, point along a direction parallel to \(k_{p}\). However, due to the symmetry of the Brillouin zone, if \(k_{\text{in}}\) lies in the plane \(k_{x} = k_{y}\), then \(k_{p}\) will also lie in this plane, as will the propagation direction of the radiation. Hence, for this particular set of input wave vectors, the propagation direction can be parameterized by a single angle. This condition holds regardless of which crystal facet is exposed. We note that the dispersion surface offers an easy way to confirm this result, which otherwise requires a more complex analysis [142, 148-150].

Figure 3.4 shows one quadrant of a two-dimensional slice through the dispersion surface of Figure 3.3(c), along the plane \(k_{x} = k_{y}\). The inset shows the complete two-dimensional slice, along with the Brillouin zone boundary in this plane. This figure illustrates an example of the construction for determining the propagating wave vector. In this example, the incident energy is \(\Omega = 0.73\) [as in Figure 3.3(c)], and the incident angle is \(\theta_{\text{in}} = 24^\circ\) relative to the surface normal (which, in this case, is the \{100\} axis). The example shown here illustrates the phenomenon of negative refraction, which has been the topic of much recent discussion [26, 151-155]. As noted previously, it is possible in a photonic crystal to have negative refraction without a negative effective
refractive index [25]. This follows because the refraction is determined by the local anisotropy of the dispersion surface, as shown in Figure 3.4. It should also be clear from this figure that a small change in the incident angle (in this case, a small increase) can move the resulting value of $k_P$ across a region of substantial curvature on the dispersion surface, leading to a very large change in the propagation angle.

Figure 3.4 One quadrant of a slice through the iso-energy surface shown in Figure 3.3(c), along the plane $k_x = k_y$. The free-space and photonic crystal dispersion surfaces are shown, along with the edge of the Brillouin zone. This diagram illustrates the construction for determining the internal propagation direction for a given input ray. The vertical dashed line represents the momentum conservation condition for the component of $k$ perpendicular to the surface normal (in this example, the $\{100\}$ axis). The incident wave vector $k_{in}$ (at an angle of 24° relative to the surface normal), the internal propagating wave vector $k_p$, and the surface gradient (denoting the propagation direction) are shown. For this particular choice of input angle, the propagating ray exhibits negative refraction. The inset (lower right) shows the full slice through the dispersion surface, along with the edge of the Brillouin zone.

Figure 3.5 shows the variation of the internal propagation angle with frequency, this time for the case of a $\{111\}$ input facet. As above, the input beam is confined in the
{110} plane, so the propagating beam is also confined in that plane and its direction is specified by a single angle. Here, we display the propagating angle $\theta_p$ for a fixed input orientation of $\theta_{\text{in}} = 39^\circ$ relative to the {111} axis, as a function of the wavelength of the incident light. At small frequencies, $\theta_p$ is constant, with a value given by Snell’s law as expected for an isotropic band structure. At high frequencies, $\theta_p < 0$, so negative refraction occurs. Near $\Omega = 0.80$, the propagation direction is a very sensitive function of frequency and there is a drastic change in the value of $\theta_p$ from negative to positive values. For an input wavelength of around 1300 nm, the angular dispersion in this region is of the order of 14°/nm. This is substantially larger than the values achieved in planar photonic crystals [138], and could prove valuable for wavelength division multiplexing.

![Graph](image)

Figure 3.5 Computed internal propagation direction as a function of frequency for an incoming beam incident on a {111} facet of the photonic crystal, at a fixed orientation of $(\theta_{\text{in}} \phi_{\text{in}}) = (39^\circ, 90^\circ)$. Since $\phi_{\text{in}} = 90^\circ$, the incident beam is in the {110} plane, and as a result the propagating beam also lies in this plane.
For beam steering applications, a relation between $\theta_p$ and $\theta_{in}$ for a particular value of frequency is needed. This result will of course depend on which crystal facet is exposed, due to the momentum conservation condition (see Figure 3.4). However, as noted above, once the dispersion surface is determined it is easy to compute the result for any chosen crystal orientation. We discuss the two relevant cases mentioned earlier, for which the \{100\} and \{111\} faces are exposed. In both cases, the angles $\theta_p$ and $\theta_{in}$ are measured with respect to the surface normal. Figure 3.6 shows the computed relation between these two angles for (a) $\Omega = 0.30$ (band #2) and (b) $\Omega = 0.73$ (band #4), for the case of the \{100\} surface. The low frequency result is, unsurprisingly, smoothly varying and is consistent with Snell’s law for the average (homogenized) refractive index. At the higher frequency, there is a sudden jump in the internal angle, from negative to positive values, at incident angles of roughly $\pm 25^\circ$. The rate of change is approximately 8 degrees for 1 degree change in the input angle. The variation of $\theta_p$ with $\theta_{in}$ is symmetric about $\theta_{in} = 0^0$ (i.e., normal incidence), as a result of the four-fold symmetry of the dispersion surface. This symmetry can be seen in the inset to Figure 3.4. In contrast, the \{111\} axis is not a symmetry axis for this dispersion surface, so the variation of $\theta_p$ with $\theta_{in}$ is not expected to be symmetric about the surface normal. Figure 3.7 shows the result for the case of the \{111\} surface; as in Figure 3.6, the low frequency result ($\Omega = 0.30$) obeys Snell’s law, while the result for a frequency higher in the band ($\Omega = 0.73$) exhibits discontinuities due to the warping of the dispersion surface. Also, we note in Figure 3.7(b), for $\theta_{in}$ near $75^0$ and $-50^0$, there are two values of the propagation angle. This is a manifestation of the birefringence effect reported in earlier works [132, 142].
Figure 3.6 Computed dependence of the internal propagation angle on the input angle. Both the input beam and the beam propagating inside the photonic crystal are confined in the $\{\overline{1}10\}$ plane. (a) $\Omega = 0.30$, (b) $\Omega = 0.73$. In both cases, the input facet is assumed to be a $\{100\}$ lattice plane. The low frequency behavior (a) is consistent with Snell’s law, whereas at high frequencies a strong angular dispersion is observed.

Figure 3.7 Same as Figure 3.6, except that the input facet is a $\{111\}$ lattice plane. Because the $\{111\}$ axis is not a symmetry axis for the dispersion surface (see inset to Figure 3.4), the result in (b) does not exhibit symmetry about $\theta_m = 0$. This result also shows multiple propagating solutions at high angles, consistent with earlier reports.

It is instructive to examine more closely the regions of high angular sensitivity, and explore the behavior for small variations in the input parameters. Figure 3.8 shows a
close-up view of the sensitive region near $45^\circ$ in Figure 3.7(b), for several different closely spaced frequencies. It is clear from this plot that, in order to observe the superprism effect, both $\theta_{in}$ and the radiation frequency need to be carefully chosen. For example, for a frequency of $\Omega = 0.8$, the extreme sensitivity to input angle occurs for an input angle $\theta_{in}$ of around $40^\circ$. A small shift in frequency, to $\Omega = 0.82$, shifts the angle at which the effect occurs to about $37^\circ$. In this case, no significant effect is observed at input angles near $40^\circ$.

![Graph](image)

**Figure 3.8** A close-up view of the situation shown in Figure 3.7(b), near the incident angle $\theta_{in} = 45^\circ$, for several closely spaced frequencies. The angle at which the superprism effect is observed is a sensitive function of the input frequency. However, the angular width of the transition region is not too sensitive.

We can also explore the sensitivity to small changes in the refractive index of the macroporous polymer medium. As with small changes in the frequency, we expect that small variations in the properties of the photonic lattice can also lead to large changes in the internal propagation angle, within a certain narrow range of parameters. Small changes in the refractive index of the polymer backbone will lead to small variations in
the curvature of the dispersion surface at a fixed frequency, which can shift the point at which the incident wave vector intersects this surface. Figure 3.9 shows a typical set of data illustrating this effect. Here, we compute the internal angle $\theta_p$ as a function of the incident light frequency, for several different values of the polymer refractive index. As the index increases by steps of less than 0.1%, the frequency at which a large angular dispersion is observed shifts systematically to lower values. Calculations show that around $\Omega = 0.80$, a maximum change of around 70° in the propagation angle is obtained for 0.63% change in the polymer index.

![Graph showing $\theta_p$ as a function of $\Omega$](image)

**Figure 3.9** Internal angle $\theta_p$ as a function of frequency, showing the sensitivity to small changes in the refractive index of the macroporous polymer backbone. In this calculation, the incident angle is fixed at $\theta_{in} = 39°$ with respect to the $\{111\}$ input facet. The eleven data curves show the result for polymer indices ranging from 1.59 to 1.60, in increments of $10^{-3}$.

This property can be applied to optical sensing. If the polymer which comprises the photonic crystal is also a recognizing agent for a certain analyte, then the presence of the analyte would lead to a small shift in the index of the photonic crystal, due to adsorption or chemical reaction with the polymer. This shift would in turn lead to a large
change in the internal propagation angle, which may be more easily detected than the corresponding shift in the wavelength of the optical stop band [18]. We note that this sort of calculation is somewhat more cumbersome than for the earlier examples, since one must compute a new dispersion surface, not only for each energy, but also for each different refractive index. Nevertheless, the procedure, once the dispersion surface is determined, remains the same. A more detailed explanation of this sensor is presented in Chapter 4.

So far, all of our illustrative results have been restricted to the case where the \( k \)-vector of the input beam lies in the plane \( k_x = k_y \), so that the internal propagating beam direction can be parameterized by a single angle. We have concentrated on this situation for ease of displaying the results. However, the superprism effect is still present even if this condition is not satisfied. As an illustration, Figure 3.10 shows a portion of the three-dimensional dispersion surface for \( \Omega = 0.73 \), along with the propagating ray and wave vector for a particular input ray. This illustrates the large out-of-plane propagation that can occur if the dispersion surface is warped. Figure 3.11 shows the calculated propagation direction for out-of-plane propagation, for a fixed orientation input ray at \( (\theta_{in},\phi_{in}) = (50^\circ,85^\circ) \), as a function of frequency. For small frequencies, the propagation beam stays in the plane of the incoming beam. But for high frequencies, both \( \theta_p \) and \( \phi_p \) are sensitive functions of frequency. There is large out-of-plane propagation and at around \( \Omega = 0.734 \), both \( \theta_p \) and \( \phi_p \) change drastically. For frequencies above \( \Omega = 0.735 \), \( \phi_p \) reaches a constant value of around 93°. This behavior may offer improvement in previously described applications since beams of slightly different frequencies would be much better resolved inside the photonic crystal. In order to observe such a large out-of-
plane propagation as shown in Figure 3.11, very thick crystals may be needed. The samples grown from colloids are typically only a few microns thick, although thicker high-quality crystals have been reported [156].

Figure 3.10 An octant of the $\Omega = 0.73$ dispersion surface (fourth band). Both $\theta_p$ and $\phi_p$ can change drastically if the incoming beam is not in the $\{110\}$ plane. This is illustrated for an input ray with $\theta_{in} = 137^\circ$ and $\phi_{in} = 89^\circ$. Only the propagation wave vector (from the $\Gamma$ point to the dispersion surface) and the propagation direction (arrow, $\theta_p = 100^\circ$, $\phi_p = 37^\circ$) are shown.

Finally, as the calculated angle and wavelength sensitivities are very large, a consideration of experimental parameters is appropriate. An experimental realization of this effect depends on the degree of collimation of the incoming beam, an issue which has been considered by Baba et al. [157]. We expect that, in order to clearly observe the extreme sensitivity of the propagation direction to the various parameters, it will be necessary for the input beam to be well collimated, so that the spread in incident angles is small compared to the angular width of the sensitive transition region. From a careful examination of Figure 3.8, we note that the width of this transition decreases for
increasing frequency $\Omega$. However, even at a frequency of $\Omega = 0.8$, the width of the transition is $\Delta \theta_{in} \sim 1^\circ$ or $\sim 17$ mrad. An angular divergence of less than 1 mrad is readily obtained using many different laser sources. Even a focused beam does not exhibit too much divergence, as long as the focal length is not too small (e.g., $f > 4$ mm for a 0.5 mm diameter input beam).

![Graph](image)

Figure 3.11 Computed internal propagation direction as a function of frequency for an incoming beam incident on $\{111\}$ face of the photonic crystal, at a fixed orientation of $(\theta_{in}\phi_{in}) = (50^\circ, 85^\circ)$. At high frequencies, the propagation beam is not confined in the plane of the incoming beam, and both $\theta_p$ and $\phi_p$ exhibit large angular dispersion.

Another factor to consider is the influence of defects and disorder, which are inevitable in self-assembled structures. The role of uncontrolled defects in a photonic crystal is a matter of much current interest [158]. In the case of typical macroporous polymer photonic crystals, the presence of disorder leads to scattering, which depletes the primary propagating mode and generates a diffuse background. This should have little impact on the measurements described here, unless the depletion of the primary mode is
substantial. As long as there is sufficient energy left in the primary mode to determine its propagation direction, the super prism effect should still be observable. In fact, one could argue that the super prism geometry described in our work is one of the few proposed applications of these materials which is largely insensitive to disorder, since it relies only on a determination of the change in location (and not on an absolute measurement of the change in amplitude) of the transmitted beam.

Chapter 5 discusses in more detail the issues regarding experimental observation of the super prism effect.

3.5 Conclusion

An analysis of the super prism phenomena for a macroporous polymer photonic crystal is presented, using a sample geometry that is readily fabricated. This method is an extension of the theory developed earlier for two-dimensional crystals, and is well suited to the study of the wide variety of complex morphologies that can be fabricated using templating techniques [105, 143]. The super prism effect is observed in regions where the band structure anisotropy is substantial, although generally only for a narrow range of input parameters. This underscores the crucial role played by theoretical computation in the exploitation of this effect. Since the phenomenon is only observable for a specific set of input orientations and laser wavelengths, a careful theoretical study is needed to properly design any experiment. The method presented here is quite flexible, in that it only requires the full band structure of the three-dimensional photonic lattice. We predict a very large angular dispersion of 14°/nm, more than sufficient for most wavelength division multiplexing applications. We also consider the possible applications of the
superprism phenomenon to optical-based chemical sensing, a more detailed explanation of which is described in the next chapter.
Chapter 4

A photonic crystal sensor based on the superprism effect

This chapter describes an optical sensing technique based on the superprism effect in macroporous polymer photonic crystals. The technique exploits the extreme sensitivity of the diffraction angle to the material properties, such as the refractive index contrast. A theoretical method for analyzing this effect is outlined, and applied to a particular sensing configuration. The sensor should provide an increase by as much as three orders of magnitude in the sensitivity to small changes in index contrast, in comparison with other optical sensing methods.

A part of this chapter is published in Reference [159].

4.1 Introduction

The development of three-dimensional photonic crystals with stop bands in the visible and near-IR has attracted much attention recently, in part because of their potential value in optical sensing applications [160]. The optical properties of these periodic media are determined by the interference of multiply diffracted waves, and are therefore very sensitive to the material parameters such as the refractive index and lattice spacing. This sensitivity can be exploited for the purposes of optical sensing, in a number of different ways. Asher and co-workers have described a colloidal crystal hydrogel thin film, which can be used for sensing a variety of analytes by observing shifts in the wavelength of diffracted light [18, 161, 162]. A related technique involves
measuring the wavelength diffracted from a volume hologram written into a chemically sensitive polymer [163]. One can also use transmission spectroscopy to observe small variations of the average refractive index within the pores of a macroporous polymer [164], an effect which has been used for biosensing applications [165]. Very recently, an ultracompact biochemical sensor based on a two-dimensional photonic crystal microcavity was demonstrated for spectral shifts corresponding to minute changes in the refractive index [166]. Change in refractive index can also be used for fluid detection through intelligent design of a photonic crystal waveguide coupler [167]. Chan et al. have described an alternate approach, based on multilayers of luminescent porous silicon with alternating porosity [168]. For most of these examples, the minimum detectable shift is on the order of a few nanometers, limited by the spectral width of the measured line. This corresponds to a change in refractive index contrast or lattice spacing on the order of 1%.

Here, we describe an optical sensor architecture based on the angular deviation of light, rather than on its spectral properties. This sensor exploits the superprism phenomenon, in which the propagation direction of a light ray inside a photonic crystal can be extremely sensitive to the material parameters of the crystal. The superprism effect has been studied extensively in recent years by a number of researchers [24, 131, 132, 135-139, 142, 169], with a primary focus on applications such as wavelength division multiplexing and optical switching [131, 142]. However, the application of this phenomenon to optical sensing, which raises a unique set of considerations, has not been explored. For example, while many groups have described the sensitivity of the effect to the incident laser wavelength [132, 137, 138, 142], none have discussed the sensitivity to
the dielectric contrast, which will be of paramount importance in sensing applications.

The use of the angular deviation of a laser for sensing offers several important advantages over other sensing techniques. It is generally much easier to detect small shifts in the position of a laser beam than it is to detect small changes in wavelength. Position-sensitive detectors can detect shifts in the centroid location of a gaussian beam as small as a few nanometers [170]; available commercial devices achieve a few tens of nanometer resolution. In contrast, small changes in the spectrum of diffracted or emitted radiation can be challenging to detect without multi-grating spectrometers, which are inefficient and difficult to align. Also, the photonic crystal sensor can in principle be integrated directly on top of the position-sensitive detector, for an extremely compact and efficient design. As described below, this method can provide orders of magnitude greater sensitivity to shifts in the refractive index of the photonic crystal material.

4.2 Numerical modeling

It is particularly advantageous to develop superprism sensors using colloidal photonic crystals, although the effect described here applies to both two- and three-dimensional photonic crystals. Using a variety of templating methods, three-dimensional photonic crystals can be formed of a wide range of materials, including polymers, ceramics, semiconductors, and even metals [20, 35, 105, 107, 143, 171]. As a result, the photonic crystal substrate can be tailored to suit the needs of a particular sensing application. Also, templated colloidal crystals possess large and accessible internal surface areas, and are therefore well suited for sensing applications.
The extreme sensitivity of propagation angle for frequencies near a photonic band edge has been recognized for a number of years [135]. Recently, several different theoretical methods have been used to describe the anomalous light propagation near a band edge, for both two-dimensional [24, 132, 136] and three-dimensional photonic crystals [131, 142]. Because we are interested in the response of the band structure to very small changes in dielectric contrast, we have adapted the method of Kosaka et al. [132], which relies on the photonic band structure rather than on numerical propagation methods described by Ochiai and co-workers [142].

Figure 4.1 shows the band structure of the type of sample to be modeled, computed using an available software package [48]. The photonic crystal is a macroporous film formed by templating a face-centered cubic (FCC) crystal of sub-micron spheres [105, 143]. When the spheres are removed, the resulting macroporous structure consists of an FCC lattice of interconnected air spheres, embedded in a dielectric matrix. In our calculations, we assume a refractive index of about 1.59 for the dielectric, approximately equal to that of polystyrene [105]. The calculation accounts for the windows between air spheres by allowing the spherical voids to overlap slightly (r/a = 0.53). Though this structure does not provide a high enough dielectric contrast for the formation of a full band gap, it does possess a substantial stop band indicative of a partial gap along the {111} crystalline axis. This is an indication of strong band structure anisotropy, which is sufficient for the observation of the superprism effect. We note that Figure 4.1 displays the band structure in the standard format, in which only the high symmetry directions are represented. To perform the computation described below, a complete band structure is required. In other words, we must calculate the band structure
from $\Gamma$ to all possible points on the surface of the Brillouin zone, not merely to the high symmetry points [131, 132]. We can of course use the symmetry of the Brillouin zone to reduce the computational load.

![Figure 4.1](image)

**Figure 4.1** The lowest eight bands in the band structure of the inverted FCC photonic crystal lattice, computed using the plane wave method [48]. The dielectric matrix has a refractive index of 1.59 (similar to polystyrene), and the air spheres overlap slightly ($r/a = 0.53$) in order to model an experimentally realizable sample. The two horizontal dashed lines represent the energies used to compute the dispersion surfaces in Figure 4.2. Inset shows the first Brillouin zone of the FCC crystal with various high-symmetry points.

From this full band structure, all possible values of wave vectors in the three-dimensional space for a particular energy can be calculated. A plot of all these wave vectors in k-space for a particular energy gives an equal-energy surface known as a dispersion surface. The shape of dispersion surface depends on the chosen value of the energy, specified by the frequency of the incident light. For small values of frequency, far from the stop band, the dispersion surface is spherical with a radius given by $c/n_{\text{ave}}$. 
where $n_{ave}$ is the average (homogenized) refractive index [131]. At higher energy values, near the photonic band gap, the band structure becomes anisotropic. As a result, the shape of dispersion surface deviates from spherical, although it retains the symmetry of the Brillouin zone. Two examples are shown in Figure 4.2.

![Dispersion Surfaces](image)

**Figure 4.2** Iso-energy (dispersion) surfaces computed from the full three-dimensional band structure (a small portion of which is shown in Figure 4.1). On the left, the dispersion surface is computed for the third band, for an energy (in dimensionless units) of 0.8. On the right, the surface for the fourth band is shown, for an energy of 0.73. The anisotropy of these surfaces gives rise to the superprism effect.

These dispersion surfaces can be used to determine the propagation direction of light inside the photonic crystal, for a specified incident light ray [131, 132]. This is accomplished by noting that the transverse component of the wave vector is conserved across the boundary of the crystal. This condition, along with the direction of the incident ray, defines a point on the dispersion surface, which is the internal wave vector. The propagation direction is obtained by computing the normal to the dispersion surface at the end point of the propagation wave vector, since the group velocity is given by $V_G = V_{k\omega}(k)$. If the dispersion surface is not spherical, then the gradient can be a sensitive function of the input parameters.
4.3 Sensor configuration

Once the internal propagation direction is determined, it is possible to compute the shift in the position of the transmitted ray if the geometry of the sample is specified. An example geometry, compatible with common fabrication methods, is shown in Figure 4.3. If the two sample surfaces are parallel, then the transmitted ray propagates parallel to the incident ray but shifted by an amount $\delta x$ that is proportional to the thickness $d$ of the film. If this shift is larger than $\sim 10$ nm, then it can be detected by a position-sensitive detector. This signal can then be used as an indicator of changes in the refractive index contrast or the lattice spacing of the photonic crystal.

Figure 4.3 A schematic of the envisioned super prism sensor. An incident laser beam lies in the plane defined by the $\{111\}$ and $\{\bar{1}1\bar{2}\}$ axes; the $\{\bar{1}10\}$ axis points out of the page. A slight change in the refractive index contrast leads to a large change in the internal propagation angle $\theta_p$, which produces a displacement $\delta x$ on a position-sensitive detector.
As an illustration, we compute the beam displacement as a function of the refractive index of the polymer for several different wavelengths. These results are shown in Fig. 4.4. In these calculations, a film thickness of 10 μm is assumed. The incident angles $\theta_{\text{in}} = 39^\circ$ and $\phi_{\text{in}} = 0^\circ$ are specified relative to the $\{111\}$ surface normal and the $\{\overline{1}12\}$ axes, respectively. Because of the symmetry of the photonic lattice, beams with $\phi_{\text{in}} = 0^\circ$ remain in the plane of incidence even inside the film [131]. These results demonstrate that substantial shifts can be expected for refractive index changes smaller than 1%, which might arise from the presence of an analyte adsorbed into the pores of the photonic lattice. Based on the aforementioned sensitivity of position-sensitive detectors, we extrapolate a minimum detectable index shift of a few parts in $10^5$. This represents roughly a factor of 1000 improvement over previous optical sensing schemes [162, 163, 168]. It should be pointed out that these calculations require computation of a new dispersion surface, not only for each energy, but also for each value of refractive index.

We note that this effect is sensitive to the wavelength of the incident light. For example, for the situation illustrated in Figure 4.4, if the spheres have a diameter of 450 nm then the specified wavelengths are spaced by ~0.33 nanometers each. This level of spectral purity can readily be achieved using a variety of commercial laser sources. Further, if the index of the polymer is slightly shifted from its nominal value, one can compensate by choosing a slightly different laser wavelength, and still maintain the high sensitivity.
Figure 4.4 Calculated beam position as a function of the refractive index of the macroporous medium, near its nominal value of 1.59 (corresponding to the index of polystyrene). The beam positions are shown relative to an arbitrary zero position, for three different incident laser wavelengths (shown in dimensionless units). This calculation is performed for incident angles of $\theta_{\text{in}} = 39^\circ$ and $\phi_{\text{in}} = 0^\circ$, and assumes a film thickness of 10 microns. At each wavelength, a beam shift of more than 10 microns is predicted for a refractive index change of less than 1%. For $\Omega = 0.8005$, the calculation has been computed for a finer step size of $\Delta n = 0.0002$, to demonstrate the linearity of the beam displacement within the transition region.

4.4 Conclusion

In conclusion, we have described a new sensing scheme that relies on the sensitivity of the propagation angle of light in a photonic crystal, rather than on its spectral properties. We discuss this new application of the superprism effect in the context of three-dimensional templated photonic crystals. These can be fabricated from an impressive array of materials, providing a wide versatility with respect to the nature of the sensing application. Since the position of a laser beam can be measured with extreme precision, this technique should provide a substantial increase in the sensitivity of optical sensing methods.
Chapter 5

Experiment for measuring superprism effect in inverted opals

This chapter describes the experimental efforts that were carried out in order to verify the theoretical results shown in Chapter 3. For the experimental realization of the superprism effect, silica spheres with diameters greater than 400 nm are required. Fabrication methods for such inverted opals are presented, and results of the superprism experiment are discussed.

5.1 Introduction

Despite numerous works on theoretical analysis of various photonic crystal structures for superprism effect [24, 131, 142, 172-181], there are very few experimental demonstrations [24, 138, 182, 183]. This is due to the narrow design window that is available for high resolution performance of the photonic crystal superprism [157, 184]. The narrow design window arises from the fact that band structure anisotropy, – the basis of superprism phenomenon –, is strongest near the photonic band edge. Therefore, the bands responsible for the superprism effect have low density of states, making the experimental observation very challenging.

Most of the superprism experiments have utilized two-dimensional photonic crystals [24, 138, 182]. There is only one example of successful demonstration of superprism effect in a three-dimensional periodic lattice [183]. This is because a good quality three-dimensional photonic crystal is very difficult to fabricate. To verify the
theoretical results of Chapter 3 through experiment, we designed an experimental setup consisting of instrumentation in optics, hardware and software. However, the primary requirement is a very good quality photonic crystal, and therefore, the fabrication methods are discussed before the explanation of the experimental setup.

5.2 Sample fabrication

The inverted opals used in the experiment are fabricated using colloidal self-assembly method. This well-established method has already been described in Chapter 2 (Section 2.3.1). In brief, a glass substrate is immersed in a colloidal solution that contains monodisperse silica particles suspended in ethanol. As the solution evaporates over ~3-4 days, capillary forces at the meniscus draw the particles together depositing them on the substrate. A schematic of this method is shown in Figure 5.1. To fabricate the inverted opal, the silica colloidal crystal is used as a template [105]. The microslide with silica colloidal crystal on its surface is covered by another microslide and dipped in ~1-2 mL of liquid monomer. The monomer used in the experiment is styrene. Capillary forces draw the liquid monomer into the void spaces between the silica particles. The monomer is then cross-linked by flood exposure to UV light. Finally, the polymer film is soaked in 2% HF acid solution to remove the silica. The resulting inverted opal photonic crystal consists of interconnected air spheres in a polymer (polystyrene) backbone. Figure 5.2 shows the schematic of the process.

For this particular superprism experiment, colloidal crystals with sphere diameters greater than 400 nm are required. The next section describes the preparation of such samples.
Figure 5.1 Schematic of the fabrication method. Silica colloids are deposited on the glass substrate by capillary forces (vertical arrow) at the meniscus between the substrate and the colloidal solution.

Figure 5.2 Procedure for making macroporous polymer. The silica photonic crystal is sandwiched between two glass slides and dipped in a monomer solution which fills its pores. The monomer is polymerized by flood exposure to UV light. The sample is then immersed in 2% hydrofluoric acid to remove the silica spheres. The resulting sample is a macroporous polymer, i.e. air spheres in a polymer background.

5.2.1 Fabrication of samples with sphere diameters greater than 400 nm

From the theoretical results presented in Chapter 3, we see that the superprism effect occurs in the range of dimensionless frequency $\Omega = 0.73 - 0.82$ (Figure 3.8). If the
laser wavelength is known, one can calculate the range of sphere diameters that could be used to fabricate photonic crystals with the required periodicity. The equation governing the required sphere diameter is \( d = 2 \times (r/a) \times (a/\lambda) \times \lambda \). Since the available laser wavelength is 532 nm and \((r/a)\) was taken as 0.53 in all the calculations, the corresponding sphere diameters are in the range of 412 nm – 462 nm for observing the superprism phenomenon \((a/\lambda = \Omega)\). It can be inferred from the equation that a laser operating at lower wavelength would be needed if we want to fabricate photonic crystals with smaller sphere size for the experiments.

In the self-assembly method of crystal fabrication, there is a competition between evaporation and sedimentation. These forces are well balanced as long as the sphere diameter is less than 400 nm. However, if the particles have size greater than 400 nm, the sedimentation forces are dominant and the deposition of particles on the substrate is not very good. Greater sedimentation forces can be compensated by introducing a convective flow to the solution, and providing a continuous flow of particles towards the meniscus region. This flow can be achieved by applying a temperature gradient across the vial [69]. The required temperature gradient is accomplished by placing the vial in a sand bath, as shown in Figure 5.3. Glass-wool is placed on top of the sand-bath to maintain a stable temperature. Once the appropriate temperature gradient is obtained (which is monitored by two thermometers), colloidal solution is poured into the vials. After initial fluctuations in the temperatures, a stable state is reached in an hour. After the temperature has stabilized, the glass substrates are inserted into the vials, and colloidal crystals are obtained in about 12 hours.
Figure 5.3  Sand-bath method. The sand-bath is covered with glass wool to maintain a stable temperature gradient across the vial. Two thermometers are used to monitor the temperature at top (65 °C) and bottom (80 °C) of the vials at all times. The figure shows three such sand baths. Drierite® is placed all around the setup to minimize the effect of moisture.

Satisfactory coating of the samples is obtained from the sand-bath method, as seen in Figure 5.4. The scanning electron micrograph of a typical sample shows that the size distribution of the spheres is not very good. Availability of silica colloidal solutions with good size distribution is still a challenge, and there are no commercial products in the market. One needs to prepare them in the lab, and the available colloidal solutions in the required size range (diameters greater than 400 nm) did not have good size distributions. Since the superprism effect utilizes the allowed modes of light, it is believed that defects in the crystal would not deplete the primary mode in a substantial way.
Figure 5.4 Typical samples formed by the sand-bath method. Left: Three samples on glass slides. Right: A scanning electron micrograph of a small portion of the crystal, showing that the size distribution of the silica spheres is not very good; and hence the photonic crystal formed is not of the very best quality.

To further check the sample quality, UV-Vis spectra of the fabricated samples are obtained by Cary 5000 spectrophotometer. The silica colloidal crystals possess a partial band gap along the [111] lattice direction, which is indicated by a peak in the UV-Vis spectrum. Figure 5.5 shows the typical UV-Vis spectra of various samples. Although a peak corresponding to the partial photonic band gap is observed, these peaks are not very strong, suggesting lack of ordering in the crystal structure. Typical samples fabricated from the sand-bath method using the available colloidal solutions produced similar UV-Vis spectra. It can be concluded that colloidal solutions with good size distributions are the primary requirement for good quality samples. Unfortunately, all the available colloidal solutions had spheres with size distributions of 8% or more, resulting in samples of not the very best quality. As the inverted opal photonic crystals are fabricated using the silica colloidal crystals as templates, the quality of the former is the same as the latter. However, as mentioned in the previous paragraph, it is believed that defects would not deplete the primary photonic mode in a substantial way, and that the superprism effect could still be observed.
Figure 5.5 Typical UV-Vis spectrum of sand-bath samples. The peaks corresponding to the partial photonic band gap are not very strong, suggesting that the photonic crystal is not of the very best quality. The legends depict sample numbers of the colloidal solutions used.

5.3 Experimental setup

Figure 5.6 shows the experimental setup for measuring the superprism effect. The crystal used in the experiment is a macroporous polymer photonic crystal, although this instrumentation is applicable to any kind of photonic crystal. The light source is a diode-pumped solid-state laser (Coherent, Model # 532) that can have a maximum output of 500 mW at 532 nm. The laser beam is green in color (λ=532 nm) and has a spot size of 4 mm for TEM\textsubscript{00} mode. Two lenses of focal lengths 15 cm and 2 cm are used for reducing the spot size to 500 μm. The photonic crystal is fixed to a manual rotation stage which is adjusted to have its axis coincide with the path of incident laser beam. This manual rotation stage is mounted on a motorized rotation stage such that the latter has its axis intersecting the incident laser beam path at right angle. This is done to make sure that the laser beam hits the photonic crystal surface at a single spot during the motion of both the
rotation stages, so that the shift in the laser beam can be measured with respect to a fixed reference point. The manual rotation stage is used to make the required crystal plane (the \{\overline{1}10\} plane) coincide with the plane of incidence, since the beam is confined in the \{\overline{1}10\} crystal plane during the superprism mechanism. If the orientation of the planes perpendicular to the \{111\} plane were known, that is, if the orientation of the \{\overline{1}12\} set of planes or the \{\overline{1}10\} set of planes were known, the manual rotation stage would not be needed. The motorized rotation stage (Newport, SR50-PP) has a resolution of 0.001° and an absolute accuracy of 0.06°. It is used to make small increments in the incident angle with respect to the photonic crystal face. The motion of this motorized stage is controlled by a GPIB compatible driver (Newport, ESP300), which feeds the increments in incident angle to the computer. The laser beam, after passing through the photonic crystal, is detected by a Position Sensitive Detector (PSD). This detector (On-trak Photonics, 2L4SP) is a duolateral two-dimensional PSD with an active area of 4 mm × 4 mm, and is capable of detecting an incident light spot position on its rectangular surface with a resolution of 250 nm. The analog output signal from the PSD is fed to a position sensing amplifier (On-trak Photonics, OT301) which is designed to provide an X-Y position output. The output from the amplifier is connected to a GPIB compatible voltmeter (Keithley 236). Through Labview®, appropriate calibration of voltage is made in terms of position, and the whole setup generates data that consists of position of the light beam after it passes through the photonic crystal as a function of the incident angle.
Figure 5.6 Experimental setup (as described in Section 5.3) for measurement of the superprism effect in inverted opal photonic crystals.

5.4 Operation

First, results are predicted for the described experimental setup so that appropriate choice of input parameters can be made in terms of best possible resolution of the output. Figure 5.7 shows expected data for a 10 μm thick crystal consisting of spheres of diameter 410 nm. The incident angle is specified relative to the [111] axis (the surface normal) of the crystal. This axis and the incident k-vector lie in the plane of the paper as shown in Figure 3.4 (Chapter 3). The beam is confined in \{\overline{110}\} plane. As the laser wavelength is 532 nm, the sphere diameter of 410 nm corresponds to a dimensionless frequency of $\Omega = 0.73$. Hence, an enormous angular deviation is expected at an incidence
angle of around 50° (Figure 3.8 of Chapter 3), which is depicted in the predicted result shown in Figure 5.7.

![Graph showing beam centroid position against incident angle](image)

**Figure 5.7** A computation of the expected experimental data. The sphere diameter and laser wavelength are assumed to be 410 nm and 532 nm respectively, and the photonic crystal is assumed to be 10 μm thick. $h$ denotes the distance between the photonic crystal and the position sensitive detector (see experimental setup in Figure 5.6)

The calculated result shows the position of beam centroid as a function of the incident angle for several different values of $h$, which is the distance between the photonic crystal and the position sensitive detector (PSD). We see that even for the smallest value of $h$ (= 1mm), the shift in the position of beam centroid is greater than 1 μm for 0.1° change in the angle of incidence. Of course, the PSD cannot be placed too far from the crystal since the shift in beam centroid would exceed the dimensions of PSD (4 mm × 4 mm). The results calculated for crystals of different sphere sizes (in the required range) show similar trend, with the effect occurring at slightly different incident angles.
These expected results allows one to choose the input parameters appropriately. For example, since the motorized rotation stage has an absolute accuracy of $0.06^\circ$ and the PSD can detect an incident light spot position with a resolution of 250 nm, the increment in incident angle can be chosen as $0.1^\circ$ for observing the superprism effect. This is because the predicted behavior is within the resolution limits of the devices for this particular value of increment.

In the experiment, the PSD is placed at about 3-4 mm away from the photonic crystal. Two parameters need to be defined for collecting data: the increment in incident angle and the scan range. The increment is taken to be $0.1^\circ$ in all scans since it is compatible with the resolution limit of the motorized rotation stage and the corresponding expected shift in the beam centroid is compatible with the resolution limit of the PSD. The scan range is chosen in accordance with the sphere size of the photonic crystal since the latter determines the region where the superprism effect is expected to occur. For example, if the sphere size is 450 nm, then the superprism effect is expected to occur at around $40^\circ$, and hence the scan range is chosen as, say, $20^\circ$ to $60^\circ$.

Another important experimental requirement is the orientation of $\{\overline{1}10\}$ set of planes with respect to the plane of incidence. This is because the superprism mechanism occurs when the beam is confined in $\{\overline{1}10\}$ set of planes, which happens when the plane of incidence and the $\{\overline{1}10\}$ set of planes are aligned. Because of symmetry of face-centered-cubic structures, the $\{\overline{1}10\}$ plane (which is perpendicular to the $\{111\}$ plane) occurs at every $60^\circ$ rotation along the [111] direction. The surface of the fabricated photonic crystals is $\{111\}$ face by default. This means that the [111] direction is the
surface normal. The crystal symmetry suggests that if the photonic crystal is rotated along its surface normal by 60° then \{\{110\} \} set of planes will be passed at least once. As it is not possible to accurately determine the orientation of these planes, the crystal is rotated using a manual rotation stage (whose axis coincides with the incident beam path) to align these planes with the incident plane. If the collected data for a particular scan range does not depict any superprism effect behavior, it means that the \{\{110\} \} set of planes is not aligned with the plane of incidence. Then the photonic crystal is rotated by a small amount using the manual rotation stage and the data is collected again for the same scan range. If the manual rotation stage is rotated by 1° after every scan, then at least 60 scans would be required for observing the expected behavior, since \{\{110\} \} plane would be aligned at least once with the incident plane because of symmetry properties.

The way data is collected is as follows. After an appropriate scan range is chosen for the photonic crystal, the scan is completed. If the data does not show any superprism behavior, then the manual rotation stage is rotated by 1° and the data is collected again for the same scan range. This step is repeated until the expected superprism behavior is observed. If the effect is not observed and the manual rotation stage has been rotated by a total of 60°, then it can be concluded that the crystal quality is not very good, and hence another sample is tried.

5.5 Results and discussion

Data was collected for macroporous polymer photonic crystals of different sphere sizes. Figure 5.8 shows a scan for a crystal with sphere size of 443 nm. For this sphere
size, enormous angular deviation is expected to occur at an incidence angle of around 42°. The plot shows shift in beam position in the $x$-direction. Shift in beam position in $y$-direction was negligible. One of the plots is for air, i.e., when there is no sample placed in front of the PSD. This helps in comparing the results when the photonic crystal is placed a few millimeters in front of the PSD. No drastic shift in the beam position is observed for the scan range of $10^\circ$ to $50^\circ$ used in this reading.

![Graph showing beam position shift](image)

**Figure 5.8** Experimental data for a free standing inverted opal photonic crystal with sphere diameter of 443 nm (green color). The shift in beam position is measured for incident angles in the range $10^\circ$ to $50^\circ$. The superprism effect was expected at around $42^\circ$. However, the expected behavior (as shown in Figure 5.7) is not observed. The photonic crystal behaves like any other standard isotropic crystal with a fixed refractive index.

Figure 5.9 shows the collected data for the same configuration except that the scan range is $20^\circ$ to $60^\circ$. Again, no drastic shift in beam position is observed. One possible reason for this may be that the $\{\overline{1}10\}$ plane is not aligned with the plane of incidence. The manual rotation stage is then rotated by $1^\circ$ and the scan is repeated.
Rotation of the sample by 1° needs to be done for the same scan till the expected superprism behavior is observed, or till the crystal has been rotated by a total of 60°.

![Graph showing x (µm) vs θ_m (degrees)](image)

**Figure 5.9** Same as Figure 5.8, but for a different scan range (20° to 60°). Superprism effect is not observed.

However, similar data is observed for all possible orientations, and for photonic crystals of different sizes. This can be attributed to poor quality of samples due to non-availability of colloidal solutions with good size distribution.

The orientation of crystal could have played some role. However, it is to be noted that the superprism effect is present even if the beam is not confined in \{\overline{110}\} plane (Figure 3.11). In that case, there is out-of-plane propagation of the light beam and a shift in the beam position in both x and y directions should have been observed. However, all the collected data showed negligible change in y direction. Basically, the sample behaved like any other standard isotropic crystal with a fixed refractive index. There was no
substantial ordering of colloidal particles and the modulation in refractive index was not good enough due to poor quality of crystals formed from the colloidal solutions. Acquiring colloidal solutions with good size distribution of silica spheres is a global issue and commercial non-availability of the same poses new challenges.

5.6 Conclusion

Though there can be various reasons for non-occurrence of superprism mechanism for the current experimental setup and conditions, the primary argument is poor quality of photonic crystals. Since there is a very narrow design window that is available for high resolution performance of the photonic crystal superprism [157, 184], samples of very good quality are required. It should be noted that there is only one instance of experimental demonstration of superprism effect in a three-dimensional photonic crystal [183].

This particular experiment can be revisited if high-quality colloidal samples become available. One option could be to use polystyrene spheres instead of silica spheres. This is because latex spheres with good size distributions are readily available commercially. Yet another option is to use a laser operating at a lower wavelength. This will allow the use of photonic crystals with smaller sphere sizes, good qualities of which are easier to obtain [68].

Chapter 8 discusses the superprism effect in a terahertz photonic crystal slab. Terahertz photonic crystals can be fabricated with essentially zero structural disorder, and therefore, are promising candidates for studying the superprism effect.
Chapter 6

Colloidal photonic crystals formed by spin-coating

This chapter describes three-dimensional colloidal photonic crystals that are formed by spin-coating monodisperse colloidal silica particles dispersed in a viscous triacrylate monomer. The spin-coating technique produces large-area colloidal photonic crystals that display a non-close-packed non-FCC lattice structure. Spectroscopic and microscopic studies, together with calculations, suggest that the colloidal particles form a non-close-packed hexagonal ABAB... type of lattice. This unconventional non-FCC lattice should enhance the functionality of the colloidal photonic crystals and could be useful for applications that require a highly porous lattice.

6.1 Introduction

Photonic crystals with a three-dimensional lattice structure are desirable because they can manipulate the propagation of electromagnetic waves in all directions [1]. Although the first three-dimensional photonic crystal was cumbersome to construct [38], a variety of techniques have been developed over the years for fabricating these structures. Promising results have been obtained from layer-by-layer micro-assembly [37, 58, 59, 185], holographic lithography [60, 61], two-photon polymerization [62], and deep x-ray lithography [63]. Three-dimensional photonic crystals with large areas can be manufactured by methods like electrochemical etching [64], auto-cloning [65], glancing-angle deposition [66], and colloidal self-assembly [20, 67-69]. With the exception of
colloidal assembly methods, all the other techniques require advanced instrumentation and are expensive to maintain. The two colloidal techniques that are most widely used are gravity sedimentation [67] and controlled drying [68]. The latter has emerged as a workhorse for preparing three-dimensional photonic crystals since it can produce large-area colloidal crystals of precisely controlled thickness in a matter of a few days. These methods, however, always yield a crystal in which the colloidal particles form a face-centered-cubic (FCC) lattice. This limits the functionality of the colloidal photonic crystals since their optical properties depend intrinsically on the lattice structure.

Recently, a new spin-coating approach has been developed that produces colloidal photonic crystals with a non-close-packed, non-FCC lattice structure [100]. Here we present microscopic and spectroscopic studies of the spin-coated photonic crystals to determine their lattice structure and characterize their structural quality. Analysis of the crystal facets using scanning electron microscopy (SEM) suggests that the colloidal particles in the spin-coated photonic crystals form a non-close-packed hexagonal ABAB... type of lattice. The transmission spectra of these crystals obtained through optical spectroscopy (UV-visible-NIR) match well with those obtained numerically by the transfer matrix method. The observations are also substantiated by the photonic band structure computed using the plane wave technique. As they possess an unconventional non-FCC lattice structure, the optical properties of the spin-coated crystals are different from those of standard colloidal crystals. As a result, spin-coated crystals offer a great promise towards enhancing the functionality of colloidal photonic crystals. Also, since the crystal geometry is non-close-packed, the lattice structure is very porous, and holds potential for microfluidic and sensing applications [18, 118, 186-188].
6.2 Sample fabrication and electron microscopy

Colloidal silica spheres with less than 5% size distribution are prepared using the Stober method [113]. Details of the spin-coating method can be found in Reference [100]. In brief, the silica particles are first dispersed in a viscous triacrylate monomer (ethoxylated trimethylolpropane triacrylate). After adding a small amount of photoinitiator (2-hydroxy-2-methyl-1-phenyl-1-propanone), the transparent dispersion is spin-coated on a silicon wafer. The thickness of the film formed on top of the wafer can be controlled by the speed and the duration of spin coating. Due to shear induced ordering [189, 190], the colloidal particles embedded in the viscous monomer are arranged in a non-close-packed non-FCC lattice structure. By flood exposing the wafer to ultraviolet light and polymerizing the monomer in less than five minutes, the crystal geometry is preserved on top of the wafer. Figure 6.1 shows the spin-coated crystals fabricated on four-inch glass and silicon wafers. To obtain these samples, silica spheres with an average diameter of 377 nm were spin-coated for three minutes at a speed of 1200 rpm. When the samples are illuminated with white light, a strong hexagonal pattern is observed, suggesting diffraction from a well-defined lattice structure with long-range crystalline order.

Figure 6.1 Spin-coated photonic crystals fabricated on 4-inch glass (left) and silicon (right) wafers. The average diameter of the silica spheres in these samples is 377 nm. The hexagonal pattern appears when the samples are illuminated with white light. The scale bar is 2 cm.
The crystals obtained by spin coating consist of silica spheres embedded in a polymer matrix. While the refractive index of silica is 1.43, that of the polymer is 1.4689 (SR-454, Sartomer, Inc). As the difference in the refractive indices is small, these silica-polymer crystals possess a low refractive index contrast, and therefore do not manifest a strong optical stop band (see Figure 6.6 below). A porous crystal with higher refractive index contrast can be obtained by selective removal of either the silica particles or the polymer matrix. Silica spheres can be etched by dipping the wafer in a 2% hydrofluoric acid solution, resulting in polymer-air crystals in about five hours. Oxygen plasma etching can be used to selectively remove the polymer to obtain the silica-air crystal. A pressure of around 1 Torr, with 400 sccm oxygen flow rate and 400 W power removes the polymer in about 25 minutes without disrupting the lattice structure. Figures 6.2(a), 6.2(b), and 6.2(c) show the three forms of the spin-coated crystals: silica-polymer, silica-air, and polymer-air crystals, respectively. It is evident from these SEM images that the lattice is non-close-packed in the plane of the substrate.

The spheres in the top layer of the crystal are arranged in a non-close-packed hexagonal pattern. We use the two-dimensional pair correlation function (PCF), \( g(r) \), to determine the center-to-center distance between the colloidal particles on the top layer [116]. The PCF is a dimensionless parameter representing the statistical mapping of the two-dimensional radial distribution of an SEM image. The first peak of the PCF denotes the mean center-to-center distance between the particles in that image. Figure 6.2(d) shows the PCF determined from the SEM image shown in Figure 6.2(b), indicating that the in-plane interparticle distance is approximately equal to 2.8 times the mean sphere radius \( r_0 \). We note that this value is very close to \( 2.828r_0 \) or \( \sqrt{2} D \), where \( D \) is the particle
diameter.

Figure 6.2 Scanning electron micrographs showing top surface of the (a) silica-polymer matrix, (b) silica-air matrix, and (c) polymer-air matrix. The scale bar in all three photographs is 3 μm. The insets at the bottom-right corners are the Fourier transforms of the corresponding images. The inset at the top-right corner in (c) is a close-up view of a small section. (d) Two-dimensional pair-correlation function (PCF) of the photograph in (b), showing that the in-plane interparticle distance is approximately equal to 2.828r_o, where r_o is the particle radius. The series of delta functions (vertical lines) represent the PCF for an infinitely extended perfect lattice.

There are two possible lattice configurations in which a crystal facet can have its constituent particles arranged in a non-close-packed hexagonal pattern, with center-to-center distance equal to \(\sqrt{2} D\). These are the [111] plane of a simple cubic lattice with \(a = D\), and the [001] plane of a hexagonal ABAB... lattice with \(a = \sqrt{2} D\) and \(c = 2D / \sqrt{3}\). These two possibilities are illustrated in Figures 6.3(a), 6.3(b), and 6.3(c). In both cases, the interparticle distance in any layer (A, B, or C) is equal to \(\sqrt{2} D\). The only difference is that the simple cubic lattice has ABCABC.... stacking of layers (along the [111] direction) whereas the hexagonal lattice has ABAB... stacking of layers (along the [001] direction). While the spheres in any one layer are non-close-packed with center-to-center
distance equal to $\sqrt{2} D$, the spheres in consecutive layers (perpendicular to the substrate) touch each other. It is difficult to distinguish between these two possibilities from only the top view SEM images. This is because the SEM cannot image effectively along the depth. An SEM image of the sample surface can show the top two layers only [Figure 6.3(d)], and would appear the same for an ABAB... structure as it would for an ABCABC... structure. It is also possible for the layers to be stacked in a random pattern of A, B, and C layers, a possibility which cannot be ruled out from top-down SEM imaging. However, cross-sectional SEM (Figures 6.4 and 6.5) indicates that such stacking faults are not common in these spin-coated crystals. This is consistent with earlier work on close-packed crystals grown by the controlled drying method, which also do not exhibit a high density of stacking faults along the growth direction [116].

To ascertain whether the packing along the crystal growth axis is ABAB... or ABCABC..., we use two approaches. The first involves cross-sectional SEM imaging to examine the stacking of the planes. The second approach involves a comparison of the experimental and calculated optical spectrum. It should be noted that the filling fraction for both the lattices are same (the spheres occupy roughly 52.3% of the total volume). Therefore, a simple application of Bragg’s law, which uses the filling fraction to determine the position of the normal-incidence reflectivity peak, cannot be used to determine the lattice structure of the spin-coated photonic crystals. A full three-dimensional photonic band structure calculation is required for precise determination of the photonic band gap position associated with each lattice configuration. First, we describe the results of our SEM imaging studies. Optical characterization is described in Section 6.3.
Figure 6.3 (a) Hexagonal unit cell with ABAB... type of lattice. The A and B layers are stacked along the [001] direction. The section highlighted in bold depicts the primitive unit cell. (b) Simple cubic unit cell. The A, B, and C layers are stacked along the [111] direction. (c) Ideal arrangement of the top two layers (A and B) in the lattices shown in (a) and (b). (d) Scanning electron micrograph showing a close-up view of the top two layers in the spin-coated photonic crystals. The scale bar is 1 μm.

The cross-sectional image of the crystal can be obtained through plasma etching [100]. Because of the non-close-packed nature of the lattice, it is very difficult to obtain a cross-section that is perfectly vertical with respect to the top surface of the crystal. Nevertheless, some cross-sectional regions are almost perpendicular to the top layer, and a careful examination of those areas reveals the packing of the layers along the crystal thickness. Figure 6.4 shows a cross-sectional SEM image of a sample that was fabricated from silica spheres with an average diameter of 325 nm. This thick crystal was prepared by spin-coating the colloidal dispersion for two minutes at 600 rpm. The crystal facet
shown in Figure 6.4 is perpendicular to the top layer of the crystal. Figure 6.5 shows the experimental cross-sectional image along with the ideal cross-sectional views of the simple cubic (ABCABC...) and the hexagonal (ABAB...) lattices. It is clear from this image that the cross-sectional pattern of the experimental sample agrees well with that of the hexagonal lattice.

Figure 6.4 Cross-sectional scanning electron micrograph of the spin-coated photonic crystal, showing a crystal facet that is perpendicular to the top face of the crystal. A magnified view of the dashed section is shown in Figure 6.5. The scale bar is 2 μm.

Figure 6.5 Left: Ideal cross-section of the simple cubic lattice with \( a = D \), where \( D \) is the sphere diameter. Middle: Magnified view of the dashed section in Fig. 4. Right: Ideal cross-section of a hexagonal ABAB... lattice with \( a = \sqrt{2} D \) and \( c = 2D/\sqrt{3} \). The crystal facets shown are perpendicular to the top layer. The cross-sectional pattern of the experimental sample (middle) matches well with that of the hexagonal lattice (right).
The lattice parameters of the crystal are determined from the cross-sectional images by measuring the horizontal and vertical center-to-center distances between the particles. The results are tabulated in Table 6-1. Three samples are fabricated from silica spheres with an average diameter of 325 nm. For each sample, a total of 200 values were extracted from cross-sectional images. The measured $a$ and $c$ values are close to the ideal values. The spheres are also aligned very well, as is evident from the very small angles between the experimental and the ideal lattice vectors. The error in the measured angles vary from 3 to 5 degrees because the minimum angular change for just one pixel variation in the horizontal or vertical directions is about 7 degrees for the measured lengths. These results strongly suggest that the lattice is hexagonal with an ABAB.... stacking.

<table>
<thead>
<tr>
<th>Measured horizontal distance, $a_m$ (nm)</th>
<th>$(a_m/a_{ideal})$</th>
<th>Angle between $a_m$ and $a_{ideal}$ (degrees)</th>
<th>Measured vertical distance, $c_m$ (nm)</th>
<th>$(c_m/c_{ideal})$</th>
<th>Angle between $c_m$ and $c_{ideal}$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 455.05 ± 36.56 0.99 ± 0.08 0.33 ± 5.65 390.69 ± 35.04 1.04 ± 0.09 0.22 ± 5.65 0.86 ± 0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 437.31 ± 31.39 0.95 ± 0.07 0.85 ± 3.29 391.35 ± 33.24 1.04 ± 0.09 0.40 ± 4.19 0.89 ± 0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 442.57 ± 30.83 0.96 ± 0.07 0.33 ± 3.64 387.81 ± 30.47 1.03 ± 0.08 0.14 ± 3.88 0.88 ± 0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6-1 Measured and ideal lattice parameters of the hexagonal unit cell. The measured values are obtained from the cross-sectional SEM images (as shown in Figure 6.4). The ideal cross-section is shown in Figure 6.5 (right). The three samples (1, 2, and 3) are fabricated from spheres with an average diameter of 325 nm.

6.3 Optical spectrum and numerical simulations

Samples fabricated on glass were used to obtain the UV-visible-NIR spectrum of the spin-coated crystals. The spot-size of the illumination beam was fixed at 1 mm.
Figure 6.6 shows typical normal incidence reflectivity spectrum (optical density) of a spin-coated crystal that was fabricated from silica spheres with an average diameter of 377 nm. The as-fabricated silica-polymer crystal does not exhibit any reflectivity peak, whereas the silica-air and the polymer-air crystals display a strong peak. This is because the refractive index contrast in the silica-polymer crystal is very low. The silica-air photonic crystal exhibits a peak at 595 nm, which is equivalent to a normalized frequency, $a/\lambda$, of 0.896. The peak for the polymer-air crystal occurs at a slightly higher wavelength (605 nm), and the corresponding normalized frequency is $a/\lambda = 0.880$. Here, the value of $a$ is assumed as $\sqrt{2}$ D, the ideal value.

![Graph showing optical density vs. wavelength for silica-air, polymer-air, and silica-polymer crystals.](image)

Figure 6.6 Typical normal incidence reflectivity spectrum (optical density) of a spin-coated photonic crystal with an average sphere diameter of 377 nm. The silica-air and polymer-air crystals exhibit a peak in their spectrum, whereas the silica-polymer crystal does not exhibit any peak due to low contrast in the refractive index. The peak position of the polymer-air crystal is at a slightly higher wavelength that that of the silica-air crystal (dotted vertical lines).
The peak positions for the silica-air and the polymer-air crystals are almost same, and can be attributed to the fact that the filling fraction of the spheres in the lattice is close to 50%. The average (homogenized) refractive index of the spin-coated crystal can be written as $n_{av} = \sqrt{\phi \times n_s^2 + (1 - \phi) \times n_b^2}$, where $n_s$ is the refractive index of the spheres, $n_b$ that of the medium in which the spheres are embedded, and $\phi$ is the filling fraction of the spheres in the unit cell. As the refractive indices of the silica spheres and the polymer are 1.38 and 1.4689 respectively, and the filling fraction is equal to 0.523, the average refractive indices for the two crystal forms are almost equal (differing by only 2.6%). Even for lattice distortions depicted in Table 6-1, the filling fraction changes by a very small amount [as explained later through Equation (6.1) and Figure 6.10]. Hence the average refractive indices for the silica-air and the polymer-air crystals remain almost equal. Thus the reflectivity peaks associated with them occur at very similar wavelengths. The peak positions can be better explained by photonic band structure calculations. Figure 6.7 shows the first Brillouin zone of the hexagonal lattice.

![Figure 6.7 First Brillouin zone of the hexagonal lattice, with all the high-symmetry points marked. The experimental data are taken at normal incidence, corresponding to the Γ-A direction in reciprocal space.](image)
The primitive lattice vectors that define the hexagonal lattice shown in Figure 6.3(a) are \( \overrightarrow{a}_1 = a \hat{i} \), \( \overrightarrow{a}_2 = -(a/2)\hat{i} + (\sqrt{3}a/2)\hat{j} \), \( \overrightarrow{a}_3 = c\hat{k} \). The lattice structure is defined by a two-atom basis. The coordinates of the basis atoms are (0,0,0) and (1/3, 2/3, 1/2). Figure 6.8 shows the photonic band structure of the non-close-packed hexagonal lattice calculated using the plane wave technique [48]. Only one lattice parameter, \( a \), is required to define the lattice structure completely since the value of \( c/a \) depends on the value of \( a \) [as explained later through Equation (6.2) and Figure 6.10]. The band structure is calculated for \( a/D = 1.3732 \), which corresponds to \( a = 0.971a_{ideal} \) and \( c/a = 0.8876 \), closely matching with the measured values shown in Table 6-1. To ensure convergence of the results, the unit cell is divided into 16 × 16 × 16 grids, with a meshing of 7 × 7 × 7 for each grid. The high symmetry points in the hexagonal Brillouin zone are defined in Figure 6.7. While the silica-polymer crystal [Figure 6.8(a)] does not exhibit any photonic band gap, several partial photonic band gaps appear when either the silica or the polymer is selectively removed [Figures 6.8(b), 6.8(c)]. From Figure 6.7, we see that the bands along the \( \Gamma-A \) direction provide information regarding the normal incidence spectrum. For the silica-air and the polymer-air crystals, the band structure predicts a narrow gap between the fourth and the fifth bands along the \( \Gamma-A \) direction [Figures 6.8(d), 6.8(e), 6.8(f)]. The gaps are centered at \( a/\lambda = 0.907 \) and \( a/\lambda = 0.870 \) for the silica-air and the polymer-air crystals, respectively. Although the peak positions predicted by the band structure are only in approximate agreement with Figure 6.6, the calculations confirm the observation that the peak position for the polymer-air crystal is at a slightly higher wavelength than that for the silica-air crystal. Deviation from ideal behavior could occur due to distortions in the lattice that are introduced during the etching process. Also, the
polymerization process increases the refractive index of the triacrylate monomer by a very small amount. This causes the calculated peak positions to be slightly different [191], and could be responsible for the small mismatch between the experimental and predicted values. The band structure of the simple cubic lattice of Figure 6.3(b) does not predict any peak at or around \( a/\lambda = 0.90 \), as shown in Figure 6.9. To characterize the other partial photonic band gaps that appear in the band structure [shaded horizontal bars in Figures 6.8(b), 6.8(c)], a more detailed spectroscopic analysis involving oblique angles of incidence would be required.

Figure 6.8  Photonic band structure of the hexagonal lattice shown in Figure 6.3(a), for (slightly different) values of lattice parameters that correspond to the estimation of Table 6-1. First twenty bands for (a) silica spheres embedded in a polymer matrix, (b) silica spheres in air background, and (c) air spheres in polymer background. The figures in (d), (e), and (f) are magnified views of the small regions between \( \Gamma \) and \( A \) points, depicted by red rectangles in (a), (b), and (c) respectively. The shaded horizontal bars in (b), (c), (e), and (f) represent partial photonic band gaps.
Figure 6.9 Photonic band structure of the simple cubic lattice shown in Figure 6.3(b). The high symmetry points R, M, and X are defined in Reference [192]. \( \Gamma-R \) corresponds to the body diagonal of the cubic Brillouin zone. The three panels show the first twenty bands for (a) silica spheres embedded in a polymer matrix, (b) silica spheres in air background, and (c) air spheres in polymer background. For \( a/\lambda \sim 0.9 \) (red rectangles), there are no (partial) photonic band gaps along the \( \Gamma-R \) direction. Shaded horizontal bars depict partial photonic band gaps along other directions.

In order to explain the earlier mentioned description concerning the filling fraction and the \( c/a \) value, Figure 6.10 shows the variation of those quantities as a function of the lattice parameter \( a \). The value of \( D \), the sphere diameter, is assumed to be a constant, so a higher value of \( a/D \) is due to an increase in the value of \( a \) only. For a hexagonal ABAB... lattice in which the spheres in the adjacent A and B layers touch each other, both the filling fraction and the \( c/a \) value can be expressed in terms of \( a/D \) through the following relations:

\[
\phi = \frac{\pi}{3 \times (a/D)^2 \sqrt{3 - (a/D)^2}} \quad (6.1)
\]

\[
c/a = 2 \times \frac{\sqrt{3 - (a/D)^2}}{\sqrt{3 \times (a/D)^2}} \quad (6.2)
\]
When the value of $a$ in a hexagonal ABAB... lattice is increased so that the lattice becomes non-close-packed ($a/D > 1$), the $c/a$ value decreases. This is because the spheres in the adjacent A and B layers that touch each other move into the void created by the non-close-packed nature of each layer. The filling fraction also decreases as the lattice becomes non-close-packed. The exact variations of these quantities are expressed by Equations (6.1) and (6.2). The dotted vertical line at $a/D = 1.3732$ in Figure 6.10 represents the value used for calculating the photonic band structure (shown in Figure 6.8). This value was chosen to be consistent with the data from Table 6-1. The corresponding filling fraction and $c/a$ values are 0.526 and 0.8876, respectively, as denoted by the dashed horizontal lines.

![Figure 6.10](image)

Figure 6.10 Variation of the filling fraction $\phi$ (left) of the spheres, and $c/a$ (right), for the hexagonal ABAB... lattice, as the lattice parameter $a$ changes from the close-packed configuration ($a/D = 1.0$) to the ideal spin-coated lattice arrangement ($a/D = 1.414$). The dashed vertical line depicts the $a/D$ value that is used for calculating the photonic band structure, whereas the dashed horizontal lines represent the corresponding $\phi$ and $c/a$ values.
It should be noted that no partial band gap along the Γ-A direction is observed for the ideal lattice structure of the silica-air and polymer-air photonic crystals (a/D=1.414). The partial band gaps open up only when the a/D value is slightly decreased, as shown in Figure 6.8(b). However, since the overlap of the bands is minimal at around $a/\lambda = 0.90$, a small and narrow transmission dip can still be expected for the ideal lattice. In order to investigate this, we compute the transmission spectrum of the ideal spin-coated crystal using the transfer matrix method [49], and compare with the observed spectrum.

Figure 6.11 shows measured normal incidence transmission spectrum for three samples, S1, S2, and S3. Sample S1 is fabricated from silica spheres of diameter 331 nm, with a size distribution of 5.27%. The average diameters of the silica spheres for samples S2 and S3 are 771 nm and 377 nm, with size distributions of 4.07% and 4.35%, respectively. The dotted curves in Figure 6.11 are the typical UV-visible-NIR spectra, which were obtained by using a spot-size of 1 mm. Similar spectra were obtained for a spot-size as small as 0.1 mm, obtained through a microscope-enhanced UV-visible spectrometer [115, 116]. The solid curves in Figure 6.11 are calculations based on the transfer matrix method. To obtain good convergence of the transfer matrix calculations, the unit cell was divided into a mesh of $9 \times 9 \times 9$, with a further sub-meshing of $10 \times 10 \times 10$ for each block in the mesh. The thickness of the crystal is assumed to be 16 layers along the [001] direction, close to that of the experimental sample. The shape of the peak and its position changes by a negligible amount when the transmission coefficients are computed for a slightly distorted lattice (a/D=1.3732). The experimental spectra matches reasonably well with the calculations. For samples S2 and S3, it can be seen that the peak positions of the polymer-air crystals shift to a slightly lower frequency, as predicted by
the band structure and the transfer matrix calculations. The shift is not evident for sample S1, probably due to higher size distribution of the spheres. All the experimental peaks are broader because the spheres are not perfectly monodisperse, and also because of defects present within the lattice [116, 193].

Figure 6.11 Transmission spectrum of (a) silica-polymer crystal, (b) silica-air crystal, and (c) polymer-air crystal. The solid curves depict the transmission coefficient calculated from the transfer matrix method. The dotted curves (vertically offset) are the typical normal incidence transmission spectra of the three different photonic crystal samples: A, B, and C, as described in the text. The position of the dips in the transmission spectra in (b) and (c) match reasonably well with the calculated dip positions (vertical dashed lines).
6.4 Conclusion

The spin-coating technique offers a fast method for fabrication of large-area colloidal photonic crystals. These crystals possess a non-close-packed, non-FCC lattice structure. Microscopic and spectroscopic studies, combined with calculations, reveal that the lattice is hexagonal ABAB... with $a = \sqrt{2} \ D$ and $c = 2D / \sqrt{3}$. The lattice structure is unconventional for colloidal crystals since it is not the standard FCC configuration. Therefore, the spin-coated crystals display different optical properties and offer a great promise in enhancing the capabilities of the colloidal photonic crystals. Finally, the non-close-packed nature of the lattice could be useful for sensing and microfluidic applications that require a highly porous lattice structure.
Chapter 7

Nanostructured virus crystals as photonic crystals for x-rays

Protein structures can be readily crystallized into lattice forms [194]. Recent advances in chemical methods have enabled the crystallization of Cowpea Mosaic Virus (CPMV) into a periodic lattice with nanometer-range ordering. The CPMV crystals provide a sturdy template for fabrication of thin films with three-dimensional morphology. As these crystals have long-range order with nanometer scale detail, they can be considered as periodic systems capable of manipulating x-ray propagation. Calculations predict that metal loaded virus crystals exhibit a normal-incidence reflectivity of 7% for wavelengths around 35 nm, which can be utilized for soft x-ray optical systems.

A part of this chapter is published in Reference [130].

7.1 Introduction

Advanced optical features exhibited by some biological organisms provide an immense opportunity for the development of biology-based optics [195, 196]. These bioorganisms can either be used as models for building adaptive optical devices [197], or exploited in template-directed fabrication [198, 199] of various nanostructures like metallic nanowires, nanofibers, and nanoparticle arrays [200, 201]. Incidentally, proteins and virus crystals play a pivotal role in structural biology and thousands of distinct
proteins have already been crystallized for high resolution crystal structure determinations in well-ordered single crystals covering a wide range of symmetries [194].

Template-directed fabrication is a powerful tool for materials design and provides an easier path for generation of patterned nanostructures. If the compositional patterns are highly ordered over large length scales, the material can exhibit strong optical diffraction useful in numerous photonic applications [202]. Fabrication of metallized thin films of Cowpea mosaic virus (CPMV) with three-dimensional morphology was reported in the year 2005 [129]. These crystals have long-range order and represent a sturdy structure with nanometer scale detail. From an optical point of view, they can be considered as periodic systems capable of manipulating soft x-ray propagation, since their unit cell dimensions are of the order of nanometers.

Here we present the metallized CPMV crystals for applications in soft x-ray optical systems. The three-dimensional network of the CPMV is advantageous since two- and three-dimensionally patterned materials provide a new set of features for the next generation of x-ray optics [203]. Not only do they offer higher performance as reflectors but they also expand functionality of optical systems beyond simple mirrors. For example, a two-dimensional diffractive component, the zone-plate, uses a series of concentric rings of specific diameters to focus x-rays [204]. Three-dimensional structures such as bent crystals [205] provide high performance mirrors for hard x-rays. More recently, superlattices of voids and gas bubbles in metals [123], formed when certain metals are implanted with inert gas ions, charged particles, or neutrons, have emerged as potential high performance monochromators at soft x-ray wavelengths [127]. Our calculations show that the CPMV crystal promises utility in mirrors and dispersive
elements on synchrotron radiation beamlines, and as active components in soft x-ray optics devices.

7.2 Virus crystal fabrication and characterization

The crystal form of CPMV was obtained more than two decades ago, but the lattice structure was solved only recently [128]. The two crystal structures of CPMV are body-centered-cubic (BCC) with \(a=31.7\ \text{nm}\), and hexagonal space group P6\(_1\)22 with \(a=45.1\ \text{nm}\) and \(c=103.8\ \text{nm}\). The BCC form of the virus crystal is studied in this work. The virus particles themselves are roughly 27.4 nm in diameter and are not perfect smooth spheres but display an icosahedral symmetry. This shape has 2-fold, 3-fold, and 5-fold symmetry axes. Because of its icosahedral shape, the dimensions of the virus particle along the three symmetry axes are not same but differ by a very small amount. In the cubic lattice structure, the 2-fold axis of the virus particle coincides with the unit cell edges, and the 3-fold axis is along the body diagonal of the unit cell.

The virus particles are not in contact along the unit cell edges but are in close contact along the body diagonal of the BCC lattice. The exact unit cell of BCC form of CPMV can be constructed using the Protein Data Bank (PDB), which has information about coordinates of each entry constituting the virus particle. Figure 7.1 shows an extended lattice consisting of four unit cells produced from the PDB file. Since it is a negative electron density map, the icosahedral virus particles are removed and the figure depicts the interconnected void spaces forming channels.

To produce optical materials active in the x-ray region, the interconnected channels are filled with metals. First, the CPMV is extracted from the leaves of California
Blackeye plant and crystallized using the vapor diffusion method [128]. The crystals are then cross-linked using glutaraldehyde as the cross-linking agent. This process makes the crystal more resistant to mechanical stress and provides a sturdy template for metallization.

![Figure 7.1](image)

**Figure 7.1** Lattice structure of the Cowpea mosaic virus (BCC) generated from the Protein Data Bank (PDB) file. Four unit cells are shown, with one of them highlighted. The virus particles appear as voids and the schematic of interconnected channels for the BCC form of virus crystal is shown.

Metal infiltration is done using the method of electroless deposition [206]. Over time, both palladium and platinum are deposited into the void spaces of the crystal structure with the quantity of the latter being five times more than that of the former, and metal infiltrated CPMV crystals representing a three-dimensional periodic and ordered structure are obtained [129]. Thin slices can be cut from the crystal using an ultramicrotome and the crystal faces can be cleaved at an appropriate angle to expose a desired crystal plane. Figure 7.2 shows transmission electron micrographs of three such lattice planes confirming the excellent internal ordering in these crystals.
Figure 7.2  TEM images depicting the lattice planes of the BCC form of the metallized CPMV crystal. Dark spots are metals and lighter color represents the virus particles. By measuring the angles between the virus particles, the crystal planes can be determined. (a) {001} plane, with schematic diagram of the particle packing across the two-fold symmetry. (b) {111} plane, and the particle packing along the three-fold axis. (c) {011} plane, and the corresponding packing. (d) The cubic unit cell depicting the cut corresponding to the data in (c). The scale is 50 nm in all figures. The insets are Fourier transforms of the corresponding images.

7.3 X-ray reflectivity of the CPMV

Calculation of the x-ray relectivity requires accurate values of optical constants for the materials constituting the virus crystals. For the soft x-ray regime, the refractive index of almost all materials varies with the x-ray wavelength. The dielectric function is not only wavelength dependent, but also has a non-zero imaginary part to incorporate absorption. Through available optical constants data [207, 208], we obtain exact values of the real (n) and imaginary (k) parts of the refractive index for the relevant wavelength range, and express the corresponding parts of the dielectric function, ε, by using standard equations: ε(real) = n^2-k^2, ε(imaginary) = 2nk.
For precise modeling of the system, it is important to define a unit cell that will represent the lattice structure of the CPMV accurately. The virus crystals that we want to analyze have three-dimensional periodicity. The unit cell consists of virus particles in body-centered-cubic configuration, and the void spaces between them are filled with platinum and palladium. The icosahedral shape of the virus particle can be modeled as a sphere since the small difference between the two forms would not substantially affect the final numerical result. Also, the virus particles can be considered as air spheres in our calculations. This is because the viral constituents are lighter materials like proteins and amino acids which scatter x-rays negligibly as compared to metals. The lattice parameter in these crystals with close-packed BCC structure is 31.7 nm. Hence, we assume the crystal lattice to consist of air spheres of diameter 27.4 nm in a BCC unit cell of lattice constant 31.7 nm, with void spaces filled with palladium and platinum.

Since both palladium and platinum have almost similar values of optical constants in the wavelength range of interest, we assume the optical constants of the infiltrated material to be an average of the two in the calculations. To justify this assumption, we graphically show the variation of optical constants of the concerned metals in the relevant wavelength range. Figure 7.3(a) and 7.3(b) depict the n and k values for platinum and palladium obtained directly from Reference [207], and the corresponding dielectric function of the two metals are shown in Fig. 7.3(c) and 7.3(d). We note that although they are wavelength dependent, the optical constants of the two metals do not differ very much in this portion of the electromagnetic spectrum. The maximum difference in the real part of the refractive index of the two metals is 0.18, while that for the imaginary part is 0.10. In our reflectivity calculations by the transfer matrix method (described later), we
also found that the results do not distinctively change whether we use the optical constants of platinum, or palladium, or their average. This is because the dielectric contrast between the virus particle (air) and the void (metal) is very low and varies very slowly along the wavelength range. Hence, in our calculations, we have taken the optical constants of the infiltrated metal to be the mean of the optical constants of platinum and palladium. This is also appropriate since the voids are filled with both the metals during the fabrication process [129].

Figure 7.3 Refractive index and dielectric function of platinum and palladium for the wavelength range of 20-50 nm. (a) Real part of the refractive index. (b) Imaginary part of the refractive index. (c) Real part of the dielectric function. (d) Imaginary part of the dielectric function. The refractive index values are obtained directly from Reference [207] (or [208]) and the dielectric constant values are calculated from the refractive index using standard equations (as described in the text).
First, to determine the crystal planes of the CPMV lattice which will produce good reflectivity peaks, we use a computational technique called the plane wave method [48]. This method assumes the refractive index of materials to be a single real value, thereby not considering absorptive effects and frequency dependence of the dielectric function. Hence, it cannot model the system precisely. However, the photonic band structure calculated from the plane wave method can still determine the crystal planes of interest and give a reasonable estimate of their peak positions. In our plane wave calculations, we assume the infiltrated material to be platinum and define its refractive index as the average of the real parts for the wavelength range of 20-50 nm. This wavelength range is chosen because the reflectivity peaks will occur in the wavelength region of order similar to the lattice constant of the CPMV crystal (31.7 nm).

Figure 7.4 shows the photonic band structure for air spheres in BCC configuration and void spaces filled with platinum. Good reflection is expected from H and P points in the Brillouin zone, which refer to \{001\} and \{111\} crystal planes respectively. This is because the bands of high and low energies meet at these points producing a small partial band gap. For other regions in the reciprocal space, the bands are almost overlapping with each other suggesting poor or no reflectivity. For the H point (\{001\} crystal plane), the normalized frequency value is around 0.9, which corresponds to a wavelength of 35 nm. Similarly for the P point (\{111\} crystal plane), the normalized frequency value is around 0.8, suggesting that x-rays impinging on \{111\} face of the crystal will produce a reflection peak at around 41 nm. These estimates of the peak positions are not exact since the plane wave method cannot incorporate frequency dependence of the refractive index. Nevertheless, the calculations ascertain that \{001\} and \{111\} crystal planes of the CPMV
lattice will produce good reflectivity peaks.

![Photonic band structure](image)

**Figure 7.4** Photonic band structure for BCC lattice of air spheres with platinum infiltrated void spaces, calculated using the plane wave method. The refractive index of platinum is taken as the average of the real parts over the entire range of wavelengths (20-50 nm). Frequency dependence or imaginary part of the refractive index is not taken into account. The inset shows the first Brillouin zone of the BCC lattice with various high symmetry points.

To calculate the x-ray reflectivity of thin film virus crystals, we use the electromagnetic transfer matrix formalism introduced by Pendry *et al.* [49]. It can consider a finite thickness of the crystal along the direction of beam propagation, and can incorporate absorption effects by assigning complex dielectric constant values as a function of frequency. Since both palladium and platinum have almost similar values of optical constants in the concerned wavelength region [207, 208], the optical constants of the infiltrated metal is taken as an average of the two. To obtain good convergence of the calculations, the unit cell is divided into a mesh of 10×10×10 blocks, with a further sub-
meshing of 10×10×10 for each block in the mesh. Figure 7.5 shows the normal incidence reflectivity peak for a metallized virus crystal thin film.

![Graph](image.png)

**Figure 7.5** X-ray reflectivity of CPMV thin film computed using the electromagnetic transfer matrix method. The virus particles crystallize in BCC structure with a lattice parameter of 31.7 nm and the void spaces are filled with palladium and platinum. The thickness of the virus crystal film is assumed to be 1 μm in the calculations. X-ray beam is considered to be normally incident on two different crystal facets: {001} and {111}.

Calculations are done for two different orientations of the top surface of the crystal - {001} plane and {111} plane. Along the direction of beam propagation, film thickness is assumed to be 1 μm, which is the typical width of the CPMV thin film crystals. For x-rays normally incident on {001} face of the crystal, a reflection peak of 4% is predicted at a wavelength of around 30 nm. The FWHM of this peak is 4 nm. On the other hand, if the x-ray beam is normally incident on {111} plane of the virus crystal, then a reflectivity of 7% is obtained at a wavelength of around 35 nm, with a FWHM of 8.5 nm. The peak positions determined by the plane wave method were overestimated by
about 5 nm because frequency dependence of the dielectric function was not taken into account. It is worth mentioning that due to high absorption by metals in this range, the reflectivity value saturates at 7% and cannot be increased by extending the film thickness. It should also be pointed out that although these virus crystal films are well-ordered, their interfacial roughness is not negligible. However, slices which are cut from the originally formed thick crystal have smooth surfaces and may eliminate the roughness damping of reflectivity peak. A normal incidence setup with appropriate signal to noise ratio will be required to observe this property.

7.4 Conclusion

We have shown that CPMV, a plant virus, can be exploited as a template for fabrication of patterned nanostructures with three-dimensional morphology. The crystals of the BCC form of the CPMV were infused with metals in an attempt to fabricate optical materials of biological origin. Calculations predict that the metal-infused crystals exhibit a normal-incidence reflectivity of 7% for wavelengths around 35 nm, which can be utilized for soft x-ray optical systems.
Chapter 8

Superprism effect in a terahertz photonic crystal slab

This chapter describes the experimental demonstration and theoretical analysis of the superprism effect in a photonic crystal slab at terahertz frequencies. For 10% variation in frequency around 0.28 THz, the refraction angle at the output facet of a wedge-shaped photonic crystal varies by about 15 degrees. A comparison with the predictions of a band structure calculation demonstrates that a three-dimensional treatment, accurately modeling the finite slab thickness and the metallic boundary conditions, is required for even a qualitative description of this experiment.

A part of this chapter is published in Reference [209].

8.1 Introduction

In recent years, the field of photonic crystal research has been one of the most active areas of optics. It is now possible to predict, with extraordinary precision, the optical properties of highly complex composite periodic structures [1]. However, in several important cases, even the most sophisticated theoretical treatments are unable to explain experimental observations. A particularly relevant example is found in the superprism effect. Several recent studies have shown significant discrepancies between experimental results and the predictions obtained from numerical simulations (e.g., finite difference time domain, FDTD) [180] and also from band structure calculations based on the plane wave expansion method [138]. The terahertz region of the spectrum is a useful
window for studying such issues, because THz photonic crystals can be fabricated with essentially zero structural disorder [210]. Indeed, it has recently been suggested that a purely two-dimensional theoretical treatment should be adequate for describing THz pulse propagation in a photonic crystal slab embedded in a parallel plate metal waveguide [211]. If correct, this would dramatically simplify the computational problem. A careful study could therefore illuminate the origin of the discrepancies in earlier superprism measurements, and provide impetus for further theoretical research.

Here we describe a study of the superprism effect at terahertz frequencies. Our sample is a photonic crystal slab, contained between a pair of parallel metal plates operating as a single-mode, broadband waveguide for TM-polarized radiation [210-212]. We observe a strong frequency dependence to the diffraction angle, as anticipated for a superprism. We explore several options for simulating the experiment, including band structure calculations for both two- and three-dimensional photonic crystals [213], and numerical modeling using both the finite element method (FEM) [214] and finite-difference time-domain (FDTD) simulations [180]. We find that all of these approaches are limited in their ability to accurately predict photonic crystal superprism experiments. We also find that a purely two-dimensional model is not useful for describing experiments such as this, in which the relevant portion of the band structure is above the light line. In the case of a metal-clad slab, these leaky modes play an important role, particularly in the THz range.

8.2 Superprism experiment
For measurement of the superprism effect, we use a photonic crystal slab which has been cut into a triangular shape (Figure 8.1). The slab consists of a periodic array of holes etched all the way through a high-resistivity silicon wafer, using deep reactive ion etching [83, 210] (see Appendix A). The crystal lattice consists of circular air holes of 360 μm diameter arranged in a hexagonal pattern, with a pitch of 400 μm. The thickness of the slab is 305 μm. The input edge facet, which is illuminated at normal incidence in our measurements, is perpendicular to the Γ-K direction of the hexagonal lattice. The opposite edge is cut at an angle of 30° with respect to Γ-K, so that the output facet is perpendicular to the Γ-M direction. This design is chosen so that the frequency-dependent angular dispersion occurs only at the slanted output facet. This triangular slab is sandwiched between two polished copper plates, cut to the same triangular shape and size, which serve as a parallel-plate metal waveguide [215]. This waveguide geometry offers both low loss and low dispersion for single-mode propagation, and has recently been used by several groups for waveguide-based terahertz spectroscopy [211, 212, 216, 217].

![Diagram](image)

Figure 8.1 Top: A photograph of the superprism. The input beam direction (Γ-K) and the output normal (Γ-M) are marked. The latter separates the region of positive and negative refraction. Bottom: A schematic of the experimental setup. The photonic crystal slab is contained between the plates of the metal waveguide. The receiver is mounted on a pivoting rail for measuring the THz radiation as a function of angle, in the far field.
Figure 8.2 Modes of the metal parallel plate waveguide, when air, silicon, or the photonic crystal (PC) slab is inserted between the plates. Dashed lines are modes of odd parity and are not be excited by external waves. Below 0.5 THz, there is only one TEM mode (TM₀) for the photonic crystal. Figure taken from Reference [97].

Figure 8.1 shows the experimental setup for measuring the angular dispersion of the transmitted radiation using THz time-domain spectroscopy. Broadband single-cycle THz pulses are generated from a photoconductive antenna, collimated, and directed to the input facet of the photonic crystal slab. Silicon plano-cylindrical lenses are used to focus the THz beam into and out of the parallel-plate waveguide. The incident electric field is linearly polarized along the axis of the cylindrical air voids, in order to excite the lowest-order TM-polarized waveguide mode.

Because of symmetry considerations and the mode spectrum of the parallel plate waveguide, no higher-order guided modes are excited for frequencies below 0.5 THz [210, 215, 218]. Thus, at all frequencies of interest in this paper, the propagation is single-mode and TEM, as seen from Figure 8.2. The THz radiation coupled into the
waveguide undergoes frequency-dependent angular dispersion at the output facet, after which it is detected by photoconductive sampling in the far field. The fiber-coupled receiver antenna is mounted on a rail which pivots around a point underneath the center of the output facet, as illustrated in Figure 8.1. The angular resolution of these measurements is determined by the aperture of the lens-coupled receiver, and is roughly 1.5°.

Figure 8.3 shows a summary of the observed spectra, obtained by Fourier transform of the measured time-domain waveforms. Here, only a small portion of the spectra are displayed, concentrating on the narrow frequency range of interest. An abrupt shift in the frequency content of the diffracted field is observed as the angle is varied over a small range, characteristic of the superprism phenomenon [24]. Figure 8.7 summarizes these experimental results (filled circles with error bars), showing a ~15° change in the refraction angle for only a 10% change in frequency. Although this value of angular dispersion is two to three times smaller than that observed in other superprism experiments [138, 182, 183], it is nevertheless much larger than the angular dispersion from a conventional optical element. In all measurements, a detectable signal could be observed only in the region of positive refraction, between the input direction and the output normal (i.e., 0° < θR < 30°).

8.3 Theoretical analysis

The physical explanation of the superprism effect is usually derived from photonic band structure calculations [24]. Figure 8.4 shows the two-dimensional band structure of our photonic crystal calculated using a plane wave expansion method [48],
assuming an infinite slab thickness. In our measurements, the superprism effect is observed in the vicinity of the edge of the second band (shaded portion in Figure 8.4). It is immediately clear that this effectively two-dimensional treatment cannot provide even a qualitative explanation of the observed results. In the relevant region of the band structure, the band curvature is negative, which implies negative angular dispersion (i.e., decreasing refraction angle with increasing frequency). This computed result is illustrated by the dashed curve in Figure 8.7. The experimental data, however, exhibits positive angular dispersion. Evidently, the band curvature in this portion of the band structure is not accurately predicted using a two-dimensional model [211].

![Graph](image)

Figure 8.3 Measured amplitude spectra of the THz radiation diffracted at several different angles. The angle $\theta_R$ is defined in Figure 8.1. The solid lines are Gaussian best fits to the data, and are shown as guides to the eye.
This result illustrates the importance of including finite thickness effects in modeling metal-clad photonic crystal slabs. We note that the portion of the band structure sampled by our measurements, which lies above the light line, is often neglected because it describes the leaky modes of the slab. However, in the case of metal cladding, such leaky modes can contribute to the measured spectra. Because of the metallic boundary conditions, even leaky modes can remain confined in the plane of the slab and propagate through the photonic crystal. This is particularly true in the terahertz regime, where ohmic losses due to the metal are much smaller than in the visible and near-infrared. Thus, in order to accurately model these experiments, the finite thickness of the slab, and its boundary conditions, cannot be ignored.

The requirement to include finite thickness effects makes the modeling of such
experiments far more challenging. The plane wave method used to calculate the two-dimensional band structure (Figure 8.4) can also be used to obtain the band structure of the photonic crystal with finite thickness, by imposing an artificial periodicity in the third dimension, with a repeat period $c$ that must be chosen arbitrarily [213]. In this approach, as the region above and below the slab are filled with air; in order to preserve this artificial periodicity, a realistic metal cladding cannot be included. The dotted lines in Figure 8.7 show the results obtained using several different values for the period $c$, corresponding to the thickness of the hypothetical air cladding. These results show that the modes above the light line are strongly affected by the choice of $c$, such that essentially any (positive) value of angular dispersion can be obtained. As a result, although it is possible to obtain reasonable agreement with the experimental results with one particular choice of $c$ (in this case, $c = 0.5$ mm), the predictive value of this method is limited [219].

Numerical methods such as FDTD and FEM are also widely used to predict the performance of photonic crystal devices [172, 220]. Although computationally cumbersome, these methods do allow for simulation of the actual device structure, including metallic boundary conditions. Even so, it has proven to be challenging to obtain good agreement with experimental results in certain cases, particularly involving superprism effects. For example, Malkova et al. have noted that FDTD calculations can strongly disagree with the predictions extracted from a photonic band structure, especially for frequencies near a band edge where the group velocity is small [180]. We encountered similar difficulties in our FDTD simulations of air-clad finite-thickness photonic crystal slab (Figure 8.5).
Figure 8.5 (a) Model of the air-clad photonic crystal slab defined in the FDTD simulations. The arrow depicts the direction of the input beam. The slab thickness is 300 μm. (b) A two-dimensional slice of the model showing the steady-state electric field distribution at 0.31 THz. The arrows denote the propagation directions of the THz waves. Outside the slanted output facet of the photonic crystal slab, the beams are very ill formed, and the superprism effect cannot be analyzed.

Finally, three-dimensional FEM calculations were used to simulate the wedge-shaped photonic crystal slab, sandwiched between metal plates. The whole structure was discretized such that the biggest mesh feature was 15 μm in the simulation domain, which resulted in a model with roughly 2.9 million mesh elements. A plane wave was launched in the Γ-K direction towards the input facet, and the output angle at the slanted facet of the crystal was extracted for each value of frequency. By noting the direction in which the electric field evolves, the output angle for any frequency can be obtained from images like the one shown in Figure 8.6. The angular dispersion, thus calculated, is shown in Figure 8.7 (open squares). As in the case of earlier superprism studies [138, 180], the agreement with the experimental measurements is only qualitative, although at least the sign of the angular dispersion is correct. The discretization limits of FEM simulations have been discussed before in the context of modeling photonic crystal devices [214].
Such results highlight the need for more sophisticated methods for simulation of complex structures containing metallic boundaries.

Figure 8.6 A two-dimensional slice of the FEM model showing the steady-state electric field distribution at 0.31 THz. The field is shown only in the region outside the photonic crystal boundary. This is because the field in the outside region is very small compared to the field inside the wedge-shaped photonic crystal, and cannot be viewed on the same scale.

Figure 8.7 Measured angular dispersion for the TM modes (filled circles with error bars). The dashed curve shows the prediction obtained using a two-dimensional band structure calculation (see Figure 8.4), while the dotted curves show the results for an air-clad two-dimensional slab with different values of the periodicity parameter c, as described in the text. The open squares depict the predicted angular dispersion obtained using a finite element method (FEM) simulation.
8.4 Conclusion

We have experimentally demonstrated the superprism effect in a photonic crystal slab at THz frequencies. The experimental results are in clear disagreement with a two-dimensional band structure calculation, indicating that a three-dimensional approach incorporating the finite thickness of the photonic crystal slab is required. Numerical methods such as FDTD and FEM are also limited in their ability to predict the device performance. We expect that these results will inspire further theoretical work directed towards the accurate computation of photonic crystal modes lying above the light line.
Chapter 9

Guided resonances in terahertz photonic crystal slabs

This chapter describes the dependence of guided resonances on the structural parameters of photonic crystal slabs. Using terahertz time-domain spectroscopy, we measure the normal-incidence transmission coefficient of photonic crystals consisting of a periodic lattice of air holes in a silicon slab. Sharp resonant features are observed in the transmission spectra due to coupling of the leaky photonic crystal modes, called guided resonances, to the continuum of free-space modes. The resonances show considerable sensitivity to the structural parameters of the slab, including the slab thickness. By varying each crystal parameter systematically, we study the dependence of the resonances on the geometry of the photonic crystal slabs. Even small changes in a parameter such as the slab thickness, for example, can lead to dramatic changes in the optical spectrum. We also compare the transmission spectrum of a photonic crystal slab with hexagonal lattice to that of a slab with a square lattice. In most cases, the experimental results match very well with numerical simulations based on the finite element method.

Portions of this chapter appear in Reference [221].

9.1 Introduction

Photonic crystals are materials with a periodically modulated refractive index in one or more dimensions [1]. They have been studied extensively due to their potential to manipulate the propagation of electromagnetic waves in a variety of novel ways [2, 3]. In
particular, photonic crystal slabs have attracted a great deal of attention because they provide a route towards development of optical architectures for integrated photonic circuits [222]. A photonic crystal slab has a two-dimensional lattice structure in the plane of the slab, and uses index guiding to confine light in the third dimension.

In the band structure of a photonic crystal slab, the modes that lie below the light line are strictly confined in the plane of the slab. These in-plane modes, called guided modes, have been exploited to implement various photonic devices [9, 213, 223-227]. In contrast to the guided modes, the photonic crystal modes that lie above the light line can leak out of the plane of the slab. These discrete leaky modes, called guided resonances, couple to the continuum of free-space modes to produce sharp resonant features in the out-of-plane transmission spectrum of the photonic crystal slab [228-230]. The resonant features exhibit an asymmetric line shape [231], characteristic of the well-known Fano resonance phenomenon observed in condensed matter systems due to interference between discrete and continuum states [232, 233].

Several studies have exploited the leaky modes in photonic crystal slabs to realize efficient light emitting devices [234-236]. The Fano resonances in photonic crystal slabs have been used to demonstrate mirrors and polarization splitters [237], and also to describe high transmission through sharp bends [238]. It has been shown that by varying the distance between a pair of closely spaced photonic crystal slabs, the guided resonances can be tuned to design optical switches, displacement sensors, and optical filters [27, 239, 240]. Report of the observation of guided resonances in asymmetrical photonic crystal slabs is very promising because of the ease of fabrication of such structures [241]. Some studies have analyzed the characteristics of the guided resonances
in crystal lattices with structural disorder [242, 243]. The dependence of the guided resonances on the angle of illumination was studied in photonic crystal slabs at visible, near-infrared, and terahertz frequencies [244-246]. A recent theoretical study used electron injection, electric field, and temperatures as parameters to control Fano resonance shift in photonic crystal slabs [247]. More recently, researchers have used air-hole photonic crystal slabs to study the properties of guided resonances as a function of the hole radius [248]. Yet, a systematic study of the variation of the optical spectra as a function of structural parameters is still lacking.

In this chapter, we present experimental and theoretical studies of guided resonances in terahertz photonic crystal slabs as a function of various crystal parameters. The photonic crystal slabs are fabricated by etching an array of holes in silicon. The normal-incidence transmission spectrum, perpendicular to the plane of the slab, is measured using terahertz time-domain spectroscopy [210, 249]. As the crystal parameters like the hole radius, the lattice periodicity, and even the slab thickness are changed, the resonant features in the transmission spectrum are observed to vary significantly. Comparison between transmission spectra of photonic crystal slabs with hexagonal and square lattice of holes is also presented. The observations show that the guided resonances are very sensitive to the lattice geometry of the crystal.

Our results also highlight the excellent correspondence between experimental measurements and numerical calculations based on the finite element method. Such agreement is notable, particularly for photonic bands lying above the light line, because these bands are very difficult to compute accurately for the case of a two-dimensional slab of finite thickness using plane wave expansion methods [209]. In our case, careful
comparisons are possible because the photonic crystals are fabricated with essentially no structural disorder and negligible surface roughness effects [243].

9.2 Experiment

A schematic of the experimental setup is shown in Figure 9.1. Single-cycle terahertz pulses are generated and detected using photoconductive antennas. To measure the normal-incidence transmission spectrum, the photonic crystal slab is placed perpendicular to the beam path. The terahertz radiation is focused into the crystal by a polyethylene lens, and a similar setup is used to collect the transmitted radiation. Using this technique, one measures the transmitted electric field as a function of time. The complex transmission coefficient of a sample is given by the ratio of the Fourier transform of a pulse transmitted through the sample to that of a reference. The reference is the freely propagating pulse measured without the sample in the beam path. This also permits a direct measurement of the spectral phase of the transmitted radiation, relative to that of the reference pulse [246]. By measuring the terahertz pulse over a 555 picosecond window, a frequency resolution of 1.8 gigahertz is obtained in the measurements.

The photonic crystal slabs consist of a hexagonal array of circular air holes in silicon. A slab with a square lattice of holes was also fabricated for comparison of the transmission spectra. The holes are etched all the way through the silicon slab using deep reactive ion etching [83, 210]. Silicon of very high resistivity ($\rho > 10$ $\text{k}$\Ohm cm) is used because of its low absorption and frequency-independent refractive index ($n = 3.418$) in the terahertz regime [250]. Each photonic crystal slab is characterized by three parameters: the hole radius $r$, the lattice parameter $a$, and the slab thickness $t$. Figure
9.2(a) shows one of the samples, with \( r = 150 \, \mu m \), \( a = 400 \, \mu m \), and \( t = 300 \, \mu m \). In all measurements presented in this paper, the electric field is polarized along the \( \Gamma-K \) direction of the hexagonal lattice, although identical results are obtained for the \( \Gamma-M \) orientation as well. For the slab with a square lattice, the electric field is polarized along the \( \Gamma-X \) direction.

Figure 9.1 A schematic of the experimental setup. The terahertz radiation propagates in the direction perpendicular to the plane of the photonic crystal slab. The terahertz beam spot size is roughly 8 mm.

Figure 9.2 (a) A top view of the photonic crystal slab with hexagonal lattice of air holes. The crystal parameters are \( r = 150 \, \mu m \), \( a = 400 \, \mu m \), and \( t = 300 \, \mu m \). The scale bar is 300 \( \mu m \). (b) Normal-incidence transmission spectrum of the photonic crystal slab shown in (a). The open black circles are experimental results, while the solid red curve is obtained from simulations based on the finite element method (FEM).
As the feature sizes in the fabricated crystals are on the order of several hundred microns, it is possible to fabricate essentially perfect crystals using standard lithographic and etching techniques. For example, a careful analysis of the variation in hole diameters across a ~1 cm area of a wafer reveals less than ±0.3% variation [243], where this uncertainty (±1 micron) corresponds to the resolution of our optical imaging system, and is therefore an upper bound. This high sample quality is important for quantitative comparisons with numerical simulations.

Figure 9.2(b) shows the normal-incidence transmission spectrum for the sample shown in Figure 9.2(a). The spectrum consists of sharp resonant features superimposed upon a smoothly varying background. The smoothly varying background is due to the Fabry-Perot oscillations that arise because of the finite slab thickness. They appear as sinusoidally changing transmission below 0.4 THz. The sharp features in the spectrum above 0.4 THz are signatures of the leaky photonic crystal modes that are excited due to normal-incidence illumination of the crystal. The widths of these resonant features represent the lifetimes of the modes. The overall spectrum is the superposition of the Fabry-Perot oscillations and the leaky photonic crystal modes. We see that the experimental results match very well with the finite elements simulations, confirming that the fabricated crystals are of essentially perfect quality.

9.3 Numerical modeling

The theoretical transmission spectra shown throughout the paper are obtained using simulations based on the finite elements method (FEM). This technique has been successfully used to analyze various photonic crystal properties [246, 251, 252] as well as
other phenomena in the terahertz range [253, 254]. The accuracy of the FEM is closely related to the quality of discretization of the model geometry. Finer discretization of the structure produces more accurate solutions, but also requires large amounts of computer memory. Therefore, it is important to construct a model geometry that not only represents the structure accurately, but can also be simulated using the available computational resources. The dashed rectangle in the bottom picture of Figure 9.3 depicts the smallest unit cell of the photonic crystal slab with a hexagonal lattice. By defining the boundary conditions appropriately, this symmetrical rectangular part can describe the two-dimensional periodicity in the plane of the slab. The top picture in Figure 9.3 shows the computational domain that was constructed to calculate the normal-incidence transmission spectrum. The thickness of the unit cell is specified as \( t \), the slab thickness. Depending on the crystal being simulated, the hole radius \( r \) and the lattice parameter \( a \) are appropriately defined in the model. The refractive index of the hole and the silicon are assigned as 1.00 and 3.418, respectively. Air regions of cross-sections similar to the unit cell are placed before and after the unit cell. Accurate results are obtained for the relevant frequency range when the thicknesses of these air regions are at least four times that of the unit cell. The top and bottom boundaries of the whole model are defined as perfect electric conductors, while the side boundaries are defined as perfect magnetic conductors. This ensures that the electromagnetic energy within the model is not lost due to absorption. It also establishes the symmetry of the unit cell required for accurate description of the in-plane periodicity of the photonic crystal slab. The whole structure is discretized using a mesh of size 20 \( \mu \text{m} \), which results in a model with roughly 0.6 million mesh elements. The arrow shown in the computational domain (Figure 9.3) indicates the
direction in which the electromagnetic radiation propagates. The electric field is polarized along the $\Gamma$-M direction of the hexagonal lattice, although similar results are obtained for $\Gamma$-K polarization. (The model geometry for the square lattice photonic crystal is described in Section 9.6). The normal-incidence transmission coefficient is obtained by taking the ratio of the integrated power at the output plane to that at the input plane. One can also calculate the phase at the output plane, and obtain the relative phase by subtracting the phase of the reference (model with no sample in the beam path) from that of the sample.

For a frequency resolution of 2 GHz over the spectral range of interest (0.1 – 0.7 THz), a typical model runs in about 22 hours on a dual-processor workstation equipped with 16 GB of RAM. Although computationally cumbersome, this method provides an extremely accurate simulation of the experiment.

![Diagram](image)

**Figure 9.3** Top: The FEM model for the hexagonal lattice photonic crystal. The electromagnetic radiation propagates in the direction indicated by the arrow. $t$ is the slab thickness. Bottom: The hexagonal lattice with high-symmetry directions marked. The dashed rectangle is a cross-section of the smallest unit cell used in the FEM simulations.
9.4 Line shape analysis

The spectrum shown in Figure 9.2(b) consists of sharp resonant features superimposed upon a smoothly varying background. The smoothly varying Fabry-Perot oscillations that form the background are more obvious at lower frequencies, below the frequency of the first guided resonance at \(-0.44\) THz. The spacing between the successive minima (or maxima) in the Fabry-Perot oscillations is governed by the thickness and the average refractive index of the slab. The sharp features in the spectrum above 0.44 THz are manifestations of the guided resonance modes of the photonic crystal slab. These discrete guided resonance modes couple to the continuum of the free-space modes to produce transmission line shapes with a Fano profile [230]. The transmission line shape of the guided resonance is asymmetric in nature, and can be written as [231, 246]

\[
I_{GR}(\omega) = \frac{\rho - \tau \cdot \Omega_j(\omega)}{1 + i\Omega_j(\omega)}
\]  

(9.1)

where \(\rho = (\tilde{n} - 1)/(\tilde{n} + 1)\) is the amplitude reflection coefficient calculated using the average refractive index (\(\tilde{n}\)) of the photonic crystal slab. For a hexagonal lattice of air holes in silicon with \(r = 150\) \(\mu\)m and \(a = 400\) \(\mu\)m, the average refractive index of the slab is, \(\tilde{n} = 2.497\) [Equation (9.6)]. \(\tau\) is the amplitude transmission coefficient, such that \(\tau^2 = 1 - \rho^2\). The normalized frequency, \(\Omega_j\), for the \(j^{th}\) resonance is given by

\[
\Omega_j(\omega) = \frac{\omega - \omega_j}{\gamma_j}
\]  

(9.2)

where \(\omega_j\) and \(\gamma_j\) are the resonant frequency and the linewidth of the \(j^{th}\) resonance, respectively. The overall transmission is the superposition of the Fabry-Perot response and the transmission due to the individual guided resonances:
\[
t(\omega) = t_{FP}(\omega) + t_{GR_1}(\omega) + t_{GR_2}(\omega) + t_{GR_3}(\omega) + \ldots.
\]
(9.3)

\[
t(\omega) = t_{FP} + \sum_{j=1}^{N} \frac{\rho - \tau \cdot \Omega_j(\omega)}{1 + i\Omega_j(\omega)}
\]
(9.4)

Each resonant feature in the experimental transmission spectrum can be described by appropriate choice of two parameters: \(\omega_j\), the resonant frequency, and \(\gamma_j\), the corresponding linewidth. Table 9-1 shows the best fitted values of \(\omega_j\) and \(\gamma_j\) for the first seven guided resonances in the spectrum shown in Figure 9.2(b). The Fabry-Perot response is calculated using the known thickness of the slab \((t = 300 \mu m)\) and the frequency-independent average refractive index \((\bar{n} = 2.497)\). The overall transmission spectrum is obtained from Equation (9.4) by substituting Equation (9.2) and using \(N = 7\). For the choice of fitting parameters shown in Table 9-1, the line shapes predicted by the simple analytical model of Equation (9.4) agree reasonably well with the experimental line shapes (see Figure 9.4).

<table>
<thead>
<tr>
<th>Resonance</th>
<th>(\omega_j) (THz)</th>
<th>(\gamma) (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.43918</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.49858</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>0.54358</td>
<td>4.00</td>
</tr>
<tr>
<td>4</td>
<td>0.55617</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>0.59377</td>
<td>10.0</td>
</tr>
<tr>
<td>6</td>
<td>0.62097</td>
<td>0.65</td>
</tr>
<tr>
<td>7</td>
<td>0.65957</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 9-1 Resonant frequencies \((\omega_j)\) and the corresponding linewidths \((\gamma_j)\) of the first seven guided resonances shown in Figure 9.2(b). These values are used to obtain the normalized frequency parameter \(\Omega_j\) [from Equation (9.2)] for each resonance, and subsequently, the transmission spectrum [from Equation (9.4)] shown in Figure 9.4.
9.5 Dependence of the resonances on the structural parameters

To harness the full potential of the guided resonances for various applications, it is important to characterize their properties. Several studies have analyzed the guided resonances in photonic crystal slabs as a function of the angle of illumination [244-246]. Theoretical as well as experimental studies have shown that the lifetimes of the resonances can be controlled by varying the radius of the holes [230, 248]. While there are theoretical predictions on how the guided resonances would change as the lattice parameter and the slab thickness are varied [245, 255] experimental demonstrations have not been reported. We study the properties of guided resonances in photonic crystal slabs for a systematic change in each crystal parameter: the hole radius $r$, the lattice parameter $a$, and the slab thickness $t$.

9.5.1 Effect of change in the hole radius $r$
Figure 9.5 shows the transmission spectra of three photonic crystal slabs, each with a different hole radius \( r \). The lattice parameter \( a \) and the slab thickness \( t \) are identical for all the samples: \( a = 400 \, \mu m \), and \( t = 300 \, \mu m \). The photonic crystal slabs have a hexagonal lattice of holes, and the hole radii of the samples in Figure 9.5 are: (a) 180 \( \mu m \), (b) 150 \( \mu m \), and (c) 125 \( \mu m \). The corresponding \( r/a \) ratios are 0.45, 0.375, and 0.3125, respectively. It is evident that the resonances shift to lower frequencies as the radius is decreased. As the \( r/a \) ratio decreases, the average refractive index of the slab increases [see Equation (9.6) below]. An increase in the average refractive index of the slab moves the photonic bands to lower frequencies. As a result, the resonances in the transmission spectra appear at lower frequencies. Another clearly evident feature is that the decrease in the hole radius causes the resonances to be sharper, signifying an increase in their lifetime within the slab. This is expected since all resonances asymptotically become true guided modes as the hole radius approaches zero. Similar results have been discussed in previous studies [230, 245, 248].

9.5.2 Effect of change in the lattice parameter \( a \)

Figure 9.6 shows the transmission spectra of three photonic crystal slabs, each with a different lattice parameter \( a \). The hole radius \( r \) and the slab thickness \( t \) are identical for all the samples: \( r = 150 \, \mu m \), and \( t = 300 \, \mu m \). The photonic crystal slabs have a hexagonal lattice of holes, and the lattice parameters of the samples in Figure 9.6 are: (a) 575 \( \mu m \), (b) 480 \( \mu m \), and (c) 400 \( \mu m \). The corresponding \( r/a \) ratios are 0.26, 0.3125, and 0.375, respectively. Figure 9.6(c) is same as Figure 9.5(b). As the lattice parameter
decreases, the resonances shift to higher frequencies, for reasons similar to those mentioned in connection with Figure 9.5.

Figure 9.5 Variation of guided resonances with the hole radii \( r \). Normal-incidence transmission spectra of photonic crystal slabs with (a) \( r = 180 \, \mu m \), (b) \( r = 150 \, \mu m \), and (c) \( r = 125 \, \mu m \). The lattice parameter and slab thickness are identical for all the samples: \( a = 400 \, \mu m \), and \( t = 300 \, \mu m \). The open black circles are experimental results, while the solid red curves are results of FEM simulations. The theoretical spectrum in (c) matches well with the experimental spectrum when \( t = 296 \, \mu m \) is used in the simulation.

Figure 9.6 Variation of guided resonances with the lattice parameter \( a \). Normal-incidence transmission spectra of photonic crystal slabs with (a) \( a = 575 \, \mu m \), (b) \( a = 480 \, \mu m \), and (c) \( a = 400 \, \mu m \). The hole radius and slab thickness are identical for all the samples: \( r = 150 \, \mu m \), and \( t = 300 \, \mu m \). The open black circles are experimental results, while the solid red curves are results of FEM simulations.
From Figures 9.5 and 9.6, it is clear that if the slab thickness is kept constant, then the shift in the spectral positions of the guided resonances due to change in either the hole radius or the lattice parameter can be partially understood by examining the corresponding change in the average refractive index, or equivalently, the $r/a$ ratio. The next subsection combines the results of Figures 9.5 and 9.6 to analyze the variation in the positions of the guided resonances as a function of the $r/a$ ratio.

9.5.3 Effect of change in the $r/a$ ratio

Figure 9.7(a) summarizes the observed shift in the positions of the first three guided resonances as a function of the $r/a$ ratio. The positions of the resonances for each sample are extracted from Figures 9.5 and 9.6. The shift in the position of each resonance is approximately linear with respect to the $r/a$ ratio, as depicted by the linear fits. For $r/a = 0.45$, the position of the first resonance is not shown. Although present in the calculated spectrum ([Figure 9.5(a)], this resonance is not observed in the experimental spectrum because its linewidth (~1 GHz, as per the calculation) is less than the resolution of the measurements. Figure 9.7(b) shows the filling fraction of the hexagonal lattice of holes ($\phi_h$) and the average refractive index of the photonic crystal slab ($\tilde{n}$) as a function of $r/a$. The curves are obtained from the relations:

$$\phi_h = \frac{2\pi \left(\frac{r}{a}\right)^2}{\sqrt{3}}$$  \hspace{1cm} (9.5)

$$\tilde{n} = \sqrt{\left(\varepsilon_{si} \times \phi_{si}\right) + \left(\varepsilon_h \times \phi_h\right)}$$  \hspace{1cm} (9.6)
where \( \varepsilon_{Si} = 11.68 \), \( \varepsilon_h = 1.00 \), and \( \phi_{Si} = 1 - \phi_h \). The dashed vertical lines are the \( r/a \) ratios of the different samples whose transmission spectra are shown in Figures 9.5 and 9.6, and correspond to \( r/a = 0.26, 0.3125, 0.375 \), and 0.45.

Figure 9.7  (a) Shifts in the positions of the first three resonances as a function of \( r/a \) (extracted from Figures 9.5 and 9.6). (b) Variation of the filling fraction of the air holes (left), and the average refractive index of the photonic crystal slab (right), as a function of \( r/a \) value of the hexagonal lattice. The dashed vertical lines depict the \( r/a \) values of the samples whose transmission spectra are shown in Figures 9.5 and 9.6.

Using the linearly fitted curves in Figure 9.7(a), the shift in the first three resonances can be quantified with respect to small changes in the \( r/a \) ratio. Table 9-2 summarizes the shifts in the positions of the resonances and the corresponding changes in \( \phi_h \) and \( \tilde{n} \), for small changes in the crystal parameters. The first row in Table 9-2 shows that a 2% change in the \( r/a \) value from 0.3125 shifts the resonance positions by 2-3%. It
also changes the filling fraction of the holes by about 4%, and the average refractive index of the slab by about 1%. If the hole radius is \( r = 125 \, \mu m \) and the lattice parameter is \( a = 400 \, \mu m \) (such that \( r/a = 0.3125 \)), then a 2% change in the hole radius (keeping the lattice parameter constant) would produce the same shifts in the resonance positions as shown in the first row of Table 9-2. However, if the hole radius is 150 \( \mu m \), then a 2% change in the hole radius would produce slightly different shifts in the positions of the resonances, as shown in the second row of Table 9-2. Instead of the hole radius, if the lattice parameter is changed by 2%, then the shifts in the resonance positions would again be slightly different (third row of Table 9-2).

<table>
<thead>
<tr>
<th>Change in ( r/a ), from 0.3125</th>
<th>Shift in resonance 1</th>
<th>Shift in resonance 2</th>
<th>Shift in resonance 3</th>
<th>Change in ( \Phi ) (%)</th>
<th>Change in ( n_{aw} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% change in ( r/a ), from 0.3125</td>
<td>10.07 GHz (3.0% change)</td>
<td>8.71 GHz (2.2% change)</td>
<td>9.28 GHz (2.1% change)</td>
<td>4.04%</td>
<td>0.98%</td>
</tr>
<tr>
<td>2% change in ( r ), from 150 ( \mu m ) (( a = 400 , \mu m ))</td>
<td>12.10 GHz (2.7% change)</td>
<td>10.46 GHz (2.2% change)</td>
<td>11.14 GHz (2.1% change)</td>
<td>4.04%</td>
<td>1.81%</td>
</tr>
<tr>
<td>2% change in ( a ), from 400 ( \mu m ) (( r = 150 , \mu m ))</td>
<td>11.86 GHz (2.8% change)</td>
<td>10.24 GHz (2.2% change)</td>
<td>10.91 GHz (2.1% change)</td>
<td>4.04%</td>
<td>1.68%</td>
</tr>
</tbody>
</table>

Table 9-2: Shifts in the positions of first three resonances for a 2% change in the \( r/a \) ratio, the hole radius, and the lattice parameter. These values are extracted from the best-fitted linear curves shown in Figure 9.7(a). Corresponding changes in the filling fraction of the air holes and the average refractive index of the photonic crystal slab are obtained from Equations (9.5) and (9.6).

In all cases, a 2% change in either the \( r/a \) ratio, the hole radius, or the lattice parameter, shifts the positions of the resonances by 2-3%. In absolute terms, Table 9-2
suggests that a 5-8 μm change in either the hole radius or the lattice parameter will shift the first three resonances by 10-12 GHz. It will also produce a 4% change in the filling fraction of the holes and change the average refractive index of the slab by less than 2%. These results indicate the degree of sensitivity of the guided resonances to the crystal parameters.

In Figure 9.7(a), all the three resonances have two data points corresponding to \( r/a = 0.3125 \). These data points are obtained from the two crystals that have different individual hole radii and lattice parameters, but identical \( r/a \) value [Figure 9.5(c) and Figure 9.6(b)]. Figure 9.8 shows a direct comparison between these two spectra. Despite having the same value of \( r/a \) and the same slab thickness, the resonances in the transmission spectra of these two crystals do not occur at the same frequencies but show a substantial difference in the spectral positions. Also, the features in the transmission spectra are not identical. We can begin to understand this observation by noting that the \( t/a \) ratios are different for the two crystals. Evidently, changes in the value of the slab thickness (normalized with respect to the lattice parameter) can produce changes in the spectral positions of the guided resonances even for crystals with the same \( r/a \) values. The \( r/a \) ratio still governs the resonant features predominantly since the two crystals display similar number of resonances within the same bandwidth. It should be noted that the slab thickness of the two samples are identical, and the difference in the \( t/a \) value is due to different lattice parameters of the crystals. To study the effect of change in slab thickness on the guided resonances, photonic crystals that differed only in the slab thickness were fabricated.
Figure 9.8 Normal-incidence transmission spectra of photonic crystal slabs with (a) \( r = 125 \) \( \mu \text{m} \), \( a = 400 \) \( \mu \text{m} \), and (b) \( r = 150 \) \( \mu \text{m} \), \( a = 480 \) \( \mu \text{m} \). These are same as Figures 9.5(c) and 9.6(b), respectively. The \( r/a \) value and the slab thickness are identical for the two samples: \( r/a = 0.3125 \), and \( t = 300 \) \( \mu \text{m} \). The open black circles are experimental results, while the solid red curves are results of FEM simulations.

9.5.4 Effect of change in the slab thickness \( t \)

Figure 9.9 shows the transmission spectra of three photonic crystal slabs, each with a different slab thickness \( t \). The hole radius \( r \) and the lattice parameter \( a \) are identical for all the samples: \( r = 150 \) \( \mu \text{m} \), and \( a = 400 \) \( \mu \text{m} \). The slab thicknesses of the samples are: (a) 300 \( \mu \text{m} \), (b) 275 \( \mu \text{m} \), and (c) 250 \( \mu \text{m} \). As the slab thickness decreases, the resonances move to slightly higher frequencies. This is because a decrease in the slab thickness increases the decay length of the guided resonance mode, lowering its effective refractive index [255]. As the guided resonance mode leaks out from the center of the slab, it decays exponentially along the direction of the incident radiation. If the slab is thinner, then the decay length in the air region outside the crystal is longer. The effective index
experienced by the mode is therefore smaller, causing it to shift towards slightly higher frequencies.

![Graph showing transmission vs. frequency for different slab thicknesses](image)

**Figure 9.9** Variation of guided resonances with the slab thickness $t$. Normal-incidence transmission spectra of photonic crystal slabs with (a) $t = 300$ μm, (b) $t = 275$ μm, and (c) $t = 250$ μm. The hole radius and lattice parameter are identical for all the samples: $r = 150$ μm, and $a = 400$ μm. The open black circles are experimental results, while the solid red curves are results of FEM simulations.

The spectral positions of the resonances can be extracted from Figure 9.9. Figure 9.10 shows the shift in the position of the first seven resonances as a function of the slab thickness. In general, the resonant frequencies shift towards slightly higher values as the slab thickness is decreased. The observed exceptions are the third and the seventh resonances for the 275 μm thick slab, although these resonances follow the expected trend in the calculated spectra. Such small differences between the experiment and the calculations are not very surprising [242, 245, 248]. The observed spectral positions of these two resonances deviate from the expected positions by only a very small amount since the rate of shift in the spectral positions of the resonances is very small (on average,
~3.6 GHz per 10 μm change in the thickness). Another feature that is evident from Figure 9.10 is that the resonant frequencies shift at different rates as the slab thickness is varied. Although the average rate of shift in the resonant frequency is very small, the resonances at higher frequencies tend to shift by larger amounts for similar variation in the slab thickness. Overall, an increase in the slab thickness moves resonances to lower frequencies, causing more resonances to appear within the same bandwidth. Similar theoretical predictions were made in an earlier study [245].

![Graph showing resonances as a function of slab thickness](image)

**Figure 9.10** Shift in the position of the first seven resonances as a function of the slab thickness $t$ (extracted from Figure 9.9).

The coupling strength of a resonance mode can drastically change as the slab thickness is varied. Figure 9.11 shows the variation in the guided resonances as a function of the slab thickness for samples with $r = 150$ μm, and $a = 480$ μm. In both the experimental as well as the calculated spectrum, the second resonance, clearly evident in the thickest and thinnest slabs, is missing in the 275 μm thick slab. This observation
suggests that a change in the slab thickness (to 275 μm) modifies the electric field distribution of the second mode in such a way that it does not couple to the external radiation modes at the frequency where the resonance should be expected (0.382 THz). The electric field patterns of the modes are known to strongly influence their coupling strengths [245, 248, 256]. Figure 9.12 shows the electric field patterns of the second resonance for the three crystals whose transmission spectra are shown in Figure 9.11. These two-dimensional plots are obtained from the FEM models. The color indicates the strength of the in-plane electric field, and the arrows denote the local field direction. For slabs of thicknesses 300 μm and 250 μm [Figures 9.12(a) and 9.12(c), respectively], the patterns of the electric field distributions are almost identical. In contrast, the second mode for the 275 μm thick slab [Figure 9.12(b)] clearly has a different electric field pattern. This fact evidently inhibits the coupling of this mode to the external field, so that it is not observed in the transmission spectrum.

![Graph](image)

**Figure 9.11** Same as Figure 9.9, but for samples with \( r = 150 \) μm, and \( a = 480 \) μm. Slab thicknesses are (a) \( t = 300 \) μm, (b) \( t = 275 \) μm, and (c) \( t = 250 \) μm.
Other subtle differences in the spectrum can also appear as the slab thickness is varied. In Figure 9.11, the non-uniform shift in the resonant frequencies with respect to the slab thickness is evident from the two resonances between 0.40 and 0.45 THz. While those two resonances can be clearly resolved in the 300 μm thick slab, they almost coalesce into one resonance as the slab thickness is decreased to 250 μm. Variation in the slab thickness also affects the lifetimes of the resonances in different ways. As the slab thickness is varied, the linewidth of a particular resonance can either increase or decrease depending on how the electric field symmetry of the mode is modified. For example, the third and the fourth resonances (between 0.40 and 0.45 THz) in Figure 9.11 become sharper as the slab thickness is decreased. In contrast, the fifth resonance (between 0.45 and 0.50 THz) first becomes broader as the slab thickness is decreased from 300 μm to 275 μm, and then splits into two broader resonances as the slab thickness is further
decreased to 250 μm. Figure 9.13 shows the normal-incidence transmission spectra as a function of the slab thickness for samples with \( r = 150 \) μm, and \( a = 575 \) μm. Again, we observe a resonance (at around 0.3 THz) which clearly becomes broader as the slab thickness is decreased. The broadest resonant feature (for the 250 μm thick slab) has the lowest Q-factor, and hence the shortest lifetime within the slab.

![Transmission spectra](image)

**Figure 9.13** Same as Figure 9.9, but for samples with \( r = 150 \) μm, and \( a = 575 \) μm. Slab thicknesses are (a) \( t = 300 \) μm, (b) \( t = 275 \) μm, and (c) \( t = 250 \) μm.

As mentioned in Section 9.2, THz time-domain spectroscopy also provides access to the spectral phase of the transmitted radiation, which can be compared to that of the reference waveform. In the low-frequency range, the relative phase increases smoothly, although nonlinearly, with increasing frequency [257]. At higher frequencies, abrupt jumps corresponding to the guided resonances are observed in the phase spectrum [246]. Figure 9.14 shows a portion of the phase spectra of the samples whose transmission spectra are shown in Figure 9.13, illustrating the abrupt jumps that arise due to the lowest
two resonances. The positions of the sudden jumps correspond to the positions of the
guided resonances. Their shift to slightly higher frequencies with the decrease in slab
thickness signifies the earlier observed trend.

![Graph showing phase difference vs. frequency for various slab thicknesses](image)

**Figure 9.14** A portion of the relative phase spectrum, for the three crystals (with \( r = 150 \) \( \mu m \), and \( a = 575 \) \( \mu m \)) whose transmission spectra are shown in Figure 9.13. The symbols are experimental results, while the solid curves are results of FEM simulations. The results for \( t = 300 \) \( \mu m \) and \( t = 275 \) \( \mu m \) are vertically offset for clarity.

From the various transmission spectra, we see that the asymmetric transmission
line shapes of the guided resonances manifest themselves in two distinct ways. The first
type is observed in the lowest resonances shown in Figure 9.13 (just above 0.25 THz),
where the transmission first drops to lower frequencies, and then jumps to a higher value
as the frequency increases across the resonance. The second type varies in an opposite
way, and is observed in the lowest resonances shown in Figure 9.9 (just below 0.45 THz).
Here, the transmission first becomes higher, and then suddenly drops to a smaller value
as the frequency increases across the resonance. These two different variations in the
transmission line shapes of guided resonances have been proposed for bistable optical transfer [258], and require resonances with very narrow linewidths.

![Graph showing transmission as a function of frequency](image)

**Figure 9.15** Calculated line shape of the lowest-frequency resonance as a function of the slab thickness, for a photonic crystal slab with $r = 150 \ \mu\text{m}$, and $a = 400 \ \mu\text{m}$ (Figure 9.9). A frequency resolution of 0.1 GHz is used in the FEM simulations.

To get an accurate estimate of the linewidth of very sharp resonances, the transmission line shapes of the lowest resonances shown in Figure 9.9 (just below 0.45 THz) are calculated using a frequency resolution of 0.1 GHz in the FEM simulations (Figure 9.15). Besides resonances moving to slightly higher frequencies, the linewidths clearly become narrow as the slab thickness is decreased. The resonance for the thinnest slab (250 $\mu\text{m}$) has the highest Q-factor (1134), and hence the longest lifetime within the slab. For the slabs of thicknesses 300 $\mu\text{m}$ and 275 $\mu\text{m}$, the line shapes are asymmetric. In contrast, the line shape for the slab of thickness 250 $\mu\text{m}$ is almost symmetric in nature. This is a manifestation of the fact that the line shapes become symmetric, and the
structure behaves as a narrowband reflector if the corresponding direct pathway transmission (Fabry-Perot response) is 100% [230]. Measurement of the transmission spectrum with a frequency resolution of 0.1 GHz (as shown in Figure 9.15) would allow characterization of narrowband switching and filtering properties of photonic crystal slabs.

9.6 Transmission spectrum of crystals with different lattice structures

The results presented in the previous sections are for photonic crystal slabs with a hexagonal lattice of air holes. A photonic crystal slab with square lattice of holes was also fabricated to study the effect of lattice structure on the guided resonances. The crystal parameters of this sample are $r = 180 \, \mu m$, $a = 400 \, \mu m$, and $t = 300$. Figure 9.16 shows the FEM model used to calculate the normal-incidence transmission spectrum of the square lattice photonic crystal slab. It is similar to the computational domain of the hexagonal lattice crystal (Figure 9.3), except for the unit cell geometry. As the unit cell of the square lattice crystal is smaller in size in comparison to the hexagonal lattice crystal, discretization of the computational domain with a 20 $\mu m$ mesh results in a model with fewer mesh elements (~0.4 million). The electric field is polarized along the $\Gamma$-X direction of the lattice, and the normal-incidence transmission coefficient is obtained by taking the ratio of the integrated power at the output plane to that at the input plane.

Figure 9.17 shows the transmission spectra of photonic crystal slabs with hexagonal and square lattices. Both samples have identical crystal parameters: $r = 180 \, \mu m$, $a = 400 \, \mu m$, and $t = 300 \, \mu m$. However, as the lattice structures are different, the filling fraction of holes is much lower in the square lattice (63.6%), in comparison to the
hexagonal lattice (73.5%). Consequently, the average refractive index of the square lattice photonic crystal slab is higher, causing the resonances to appear at lower frequencies.

Figure 9.16 Same as Figure 9.3, but for a square lattice.

Figure 9.17 Normal-incidence transmission spectra of photonic crystal slabs with (a) Hexagonal lattice, and (b) Square lattice. The crystal parameters are identical for the two samples: $r = 180 \, \mu m$, $a = 400 \, \mu m$, and $t = 300 \, \mu m$. The open black circles are experimental results, while the solid red curves are results of FEM simulations.
9.7 Conclusion

In summary, the normal-incidence transmission spectra of photonic crystal slabs with air holes in silicon are measured using terahertz time-domain spectroscopy, and calculated using finite elements simulations. The Fano line shapes of the resonant features in the transmission spectrum can be described by a simple analytical model that considers coupling of discrete and continuum modes of the photonic crystal slab. The variation in the spectral positions of these resonant features is studied as a function of crystal parameters like the hole radius, the lattice parameter, and the slab thickness. The transmission spectrum of a photonic crystal slab with hexagonal lattice of holes is also compared to that of a photonic crystal slab with square lattice of holes.

The spectral positions of the resonances are most sensitive to changes in the $r/a$ ratio, which changes the average refractive index of the slab. Observations show that the resonances are quite sensitive to the hole radius and the lattice parameter, and even a small 2% change in either of the parameters can shift the spectral position of the resonances slightly, as well as change the line shape. In contrast, the shifts in the positions and line shapes of the resonances are relatively smaller, although still not negligible, for variations in the slab thickness. In general, increasing the slab thickness moves the resonances to slightly lower frequencies, causing more resonances to appear within the same bandwidth. A change in the slab thickness can also increase or decrease the lifetimes of the modes. A comparison of the transmission spectra of slabs with identical structural parameters but different lattice structures (square and hexagonal) shows that the occurrence of resonant features at relatively lower frequencies in the
square lattice can be explained by considering the effects of the average refractive index. These results should inspire further interest in the development of photonic devices based on guided resonances.
Chapter 10

The effect of structural disorder on guided resonances

This chapter describes the effect of structural disorder on guided resonances in terahertz photonic crystal slabs. The photonic crystal slabs consist of a hexagonal array of air holes in silicon. The normal-incidence transmission coefficient of the photonic crystal slabs is measured using terahertz time-domain spectroscopy. The transmission spectra exhibit sharp resonant features with Fano line shapes. They are produced due to the coupling of the leaky photonic crystal modes, called guided resonances, to the continuum of free-space modes. The results indicate that the resonant features are very tolerant to disorder in the hole diameter, but very sensitive to disorder in the lattice periodicity.

Portions of this chapter appear in Reference [243].

10.1 Introduction

Photonic crystals are materials with a periodically varying refractive index [1, 5, 30]. The refractive index can vary in one or more dimensions, so that photonic crystals can manipulate the flow of electromagnetic waves in a variety of novel ways [1]. In particular, a photonic crystal slab has a two-dimensional lattice structure in the plane of the slab, and uses index guiding to confine light in the third dimension [1, 213]. Because of their two-dimensional periodicity, photonic crystal slabs are capable of supporting in-plane modes, called guided modes. These guided modes lie below the light line in the photonic band structure, and are strictly confined in the plane of the slab. They have been
studied extensively and used to implement various waveguide structures and photonic devices [1, 9, 222, 223, 259].

Besides the in-plane guided modes, photonic crystal slabs also exhibit modes that can leak out of the plane of the slab and interact with the external radiation modes. These discrete photonic crystal modes lie above the light line, and are called leaky modes or guided resonances [230, 260]. They couple to the continuum of free-space modes to produce sharp resonant features in the optical transmission spectrum of the slab. This is an example of an interference phenomenon between discrete and continuum states, with the well-known Fano resonance line shape [232] often observed in atomic physics and condensed matter systems [233]. The Fano resonances in photonic crystal slabs [231] have been the subject of several recent studies [240, 241, 245-248, 255, 261]. Analogous to changes in Fano lines shapes due to impurities in the condensed matter lattice models [262], the Fano line shapes in photonic crystals can also be controlled by doping [263]. It has also been shown that resonances otherwise not present in the perfect photonic crystal [256] can appear due to lattice disorder [242].

The subject of using controlled lattice defects to engineer photonic crystal properties has always been very important [264-266]. However, a perfectly periodic dielectric structure could also be disturbed due to the presence of unintentional lattice disorder, affecting both the in-plane guided modes and the out-of-plane guided resonances. Disorder of this kind can occur due to imperfect fabrication processes, and can appear as irregularities in the size, shape, and position of the structural elements of the photonic crystal [267]. There have been numerous theoretical and experimental studies on the effect of disorder in one-dimensional [268], two-dimensional [252, 269-
279], and three-dimensional photonic crystals [116, 193, 280, 281]. All of these disorder studies, including those on photonic crystal slabs, have analyzed how the in-plane guided modes and band gaps are affected. The effect of structural disorder on out-of-plane propagation in a one-dimensional photonic crystal was presented only very recently [282]. There is also only one existing report considering the effects of weak structural disorder on guided resonances [242]. A detailed study on how lattice disorder affects the out-of-plane propagation is lacking.

We systematically evaluate the effect of several different types of lattice disorder on guided resonances in terahertz photonic crystal slabs. The photonic crystal slabs have a hexagonal lattice of air holes in silicon, and are fabricated by standard microfabrication techniques. The normal-incidence transmission spectrum, perpendicular to the plane of the slab, is measured using terahertz time-domain spectroscopy [210, 249]. We study the effects of inhomogeneity in the size of the holes as well as sub-wavelength-scale surface roughness. We also study the effect of disruption of the periodicity of the photonic lattice, resulting from displacement of the hole centers. These data reveal that the guided resonances are tolerant to disorder in the hole diameter and to interface roughness, but are very sensitive to disorder in the lattice periodicity.

10.2 Experiment

A schematic of the experimental setup is shown in Figure 10.1. Single-cycle terahertz pulses are generated and detected using photoconductive antennas. The terahertz radiation propagates in a direction perpendicular to the plane of the photonic crystal slab, and is focused into the crystal by a polyethylene lens. A similar setup is used
to collect the transmitted radiation. Using this technique, one measures the transmitted electric field as a function of time. The complex transmission coefficient of a sample is given by the ratio of the Fourier transform of a pulse transmitted through the sample to that of a reference, which is usually the freely propagating pulse, measured without the sample in the beam path. In our measurements, a frequency resolution of 1.8 gigahertz is obtained by scanning the terahertz pulse over a 555 picosecond window. In all the measurements presented in this paper, the electric field is polarized along the Γ-K direction of the hexagonal lattice, although identical results are obtained for the Γ-M orientation.

![Diagram of experimental setup](image)

**Figure 10.1** A schematic of the experimental setup. The terahertz radiation propagates in the direction perpendicular to the plane of the photonic crystal slab. The terahertz beam spot size is roughly 8 mm. The samples are all very thin compared to the Rayleigh range of the focused THz beam.

The photonic crystal slabs consist of a hexagonal array of circular holes etched all the way through a high-resistivity ($\rho > 10$ kΩ cm) silicon slab, using deep reactive ion etching [83, 210]. High-resistivity silicon is chosen because of its low absorption and frequency-independent refractive index ($n = 3.418$) in the terahertz regime [210, 250]. Each photonic crystal slab is characterized by three parameters: hole radius $r$, lattice
parameter $a$, and slab thickness $t$. Figure 10.2 shows one of the samples, with $r = 150 \, \mu \text{m}$, $a = 400 \, \mu \text{m}$, and $t = 250 \, \mu \text{m}$. As the feature sizes are in the order of several hundred microns, it is possible to fabricate crystals with essentially perfect structures using standard lithographic and etching techniques.

Figure 10.2 (a) A top view of the photonic crystal slab. The scale bar is 5 mm. (b) A magnified portion from (a), with a scale bar of 300 $\mu$m. The crystal parameters of this sample are $r = 150 \, \mu \text{m}$, $a = 400 \, \mu \text{m}$, and $t = 250 \, \mu \text{m}$.

Figure 10.3 shows the normal-incidence transmission spectrum for the sample shown in Figure 10.2. The overall spectrum is the superposition of two different responses: the Fabry-Perot oscillations that are prominent at lower frequencies and arise because of the finite slab thickness, and the photonic crystal modes above the light line that are excited due to normal incidence illumination of the crystal. The sudden dips in the spectrum depicted by transmission minima are the signatures of the guided resonances [230, 246]. The widths of these resonant features represent the lifetimes of the modes. We see that the experimental results match very well with the finite elements simulations [221, 246], confirming that the fabricated crystals are of essentially perfect quality.
10.3 Effect of disorder in the hole diameter

In photonic crystal slabs formed by etching of cylindrical holes into the silicon substrate, the diameter of the holes can be nonuniform if the etching conditions are not appropriately optimized. Also, the walls of the etched silicon may not be perfectly vertical and can display surface roughness. We have studied several such samples, either with diameter nonuniformity or interface roughness. In both cases, the lattice periodicity was not perturbed; the centers of the holes remained periodic on a hexagonal lattice with $a = 400 \ \mu m$.

10.3.1 Disorder in hole size

Figure 10.4 shows histograms depicting the distributions of the values of the hole diameters for one nominally perfect and two imperfect samples. These are obtained by
acquiring 25 high-resolution images of each sample, and then using image processing software to extract the individual hole diameters. The diameters of about 400 holes are measured for each of the three samples, since the experimental terahertz beam of 8 mm spot size covers about this many holes. For the perfect sample, all the holes have nearly identical diameters of 297 ± 1 microns. In the imperfect samples, the hole diameters are not uniform. Although most of the hole diameters are close to the target size (300 μm), there is a finite distribution of holes of different sizes. It can also be seen from the images that holes of almost half the ideal size occur every 2-3 mm.

Figure 10.4 Distribution of the hole diameter for perfect (top) and imperfect (middle and bottom) samples. The perfect sample has a mean hole diameter of 297 μm, which is close to the design parameter of 300 μm. The three samples have hole diameters with standard deviations of 1 μm, 32 μm, and 39.6 μm, from top to bottom. The samples in the lower two images have different slab thicknesses. The bin size of each bar in the histogram is 5 μm. Images show sample regions within a 8 mm circular area, roughly equal to the THz beam spot size. All scale bars are 1.5 mm.
Figure 10.5(a) shows the transmission spectrum of the perfect sample with $r = 150$ µm, $a = 400$ µm, $t = 250$ µm, and also of the imperfect sample shown in second row of Figure 10.4. The resonances in the imperfect crystal are only very slightly broadened and shifted in frequency, but clearly well-defined resonances remain. Similar behavior [Figure 10.5(b)] is observed in a sample with slightly different slab thickness ($t = 275$ µm) shown in the last row of Figure 10.4. The small shifts in the spectra can be attributed to the fact that the variable hole size produces a small shift in the average refractive index of the photonic crystal slab. This results in a small shift of the photonic bands, which in turn shifts the resonances by a small amount [242].

![Graphs showing transmission spectra](image)

**Figure 10.5** Normal-incidence transmission spectra of photonic crystal slabs with disorder in the hole size. (a) The solid black curve is the transmission spectrum of the ideal crystal with $r = 150$ µm, $a = 400$ µm, and $t = 250$ µm (top picture, Figure 10.4), while the dashed red curve is the spectrum of the corresponding imperfect sample (middle picture, Figure 10.4). (b) Same as (a) but for a sample with slightly different slab thickness of 275 µm. The corresponding imperfect sample is shown in Figure 10.4 (bottom picture).

It has been shown that broader resonances with low Q-factors are not substantially affected by lattice disorder [242]. But from Figure 10.5, it is clear that even the sharpest resonances are not adversely affected. This degree of tolerance to disorder in the hole size suggests that the size of the air holes is not the critical factor in determining the lifetime
of the Fano resonance modes. Similar results were observed in photonic crystal slabs at visible and infrared frequencies that exhibited very small fabrication disorders [245].

10.3.2 Disorder in hole shape

In addition to nonuniformity in hole diameter, a poorly optimized deep etching process can also lead to substantial surface roughness on the internal air-silicon interfaces within the etched holes. Figure 10.6 shows top-view images of a nominally perfect photonic crystal, as well as a photonic crystal with roughness disorder. From the image in the third column of Figure 10.6(b), it is clear that the length scale of the boundary roughness is about 20 μm. This value is small compared to the wavelength of the incident terahertz radiation, ranging from about λ/15 to λ/150 within the measured spectral band. Even so, the impact of this relatively small degree of interface roughness on the optical spectrum is not immediately obvious. For example, Maskaly et al. studied the effects of interface roughness on a one-dimensional photonic crystal, showing that the change in reflectivity can be a sensitive function of the degree of roughness [283]. In photonic crystal fibers, interfacial roughness can be the dominant loss mechanism [284].

Figure 10.7 shows the transmission spectrum of the perfect and imperfect crystals shown in Figure 10.6. We notice that for the sample that has holes with rough boundaries, the lowest two resonances at 0.436 THz and 0.472 THz are shifted by 8.3 GHz and 13 GHz, respectively. These shifts, although very small, are very reproducible. As the holes with rough boundaries are still almost circular and do not differ in sizes by large amounts, one can measure their diameters and assign an average diameter to the whole sample. Using the same analysis method described above (Figure 10.4), we find that the
average hole diameter of the sample with rough boundaries is about 4.7 µm more than that of the nominally perfect sample. This difference in diameter is very small, only about 1%. However, from a detailed study on how the resonant peaks shift in frequency with change in the hole diameter [221], a 4.7 µm difference in the hole diameter is predicted to shift the aforementioned resonances by about 11.8 GHz and 14.7 GHz, respectively. Within experimental limits, the observations are very close to this prediction. Very small but observable shifts in the resonant features for less than 4% change in the hole diameter can also be extrapolated from the studies on chalcogenide photonic crystals at near-infrared frequencies [248].

![Figure 10.6](image-url)

Figure 10.6 Top-view images of photonic crystal slabs showing disorder in the hole shape. Images from left to right increase in magnification. (a) Sample with nominally perfectly circular holes, of diameter 250 µm. (b) Sample with holes of imperfectly circular shape, exhibiting air-silicon interface roughness.
Figure 10.7 Normal-incidence transmission spectra of photonic crystal slabs with $r = 125 \, \mu m$, $a = 400 \, \mu m$, and $t = 300 \, \mu m$. The solid black curve is for the sample with perfectly circular holes [shown in Figure 10.6(a)], while the dashed red curve is for a sample with slight disorder in the hole shape [shown in Figure 10.6(b)].

Therefore, the frequency shifts observed in the transmission spectrum of the imperfect sample can be attributed to the slight difference in the average hole diameter. Provided that the surface roughness is small compared to the wavelength of the radiation, the only outcome of the rough hole boundaries is to produce a slight difference in the average hole diameter. This in turn causes the resonances to shift in frequencies by a very small amount. The resonances at higher frequencies shift by larger amounts, as observed in the detailed study of guided resonances in terahertz photonic crystal slabs [221]. In any event, it is clear that the overall features of the narrow and pronounced guided resonances are largely insensitive to the presence of moderate amounts of surface roughness.
10.4 Effect of disorder in the lattice parameter

As noted above, in the samples with lattice disorder due to imperfect shape and size of the holes, the long-range crystal periodicity is maintained. This is because the hole centers are not displaced from their ideal lattice sites. To study the effect of crystal disorder caused by disruption of the lattice periodicity, randomness in the hole positions are required. Figure 10.8 shows samples that were designed to have disorder in the lattice periodicity. The lattice parameter of the nominally perfect crystal is (i.e. the center-to-center distance between adjacent holes) \( a = 400 \, \mu\text{m} \). For the imperfect samples, the hole centers are randomly displaced by values either in the range 0-50 \( \mu\text{m} \) [Figure 10.8(b)], or in the range 0-80 \( \mu\text{m} \) [Figure 10.8(c)]. There is no disorder present due to hole shape and size: the hole diameter in all the samples are 250 ± 1 microns, and the sidewalls of the etched silicon are perfectly smooth and vertical within our ability to measure them.

The extent of disorder in the lattice parameter can be quantified by calculating the pair correlation function (PCF), \( g(r) \), from the sample images. The PCF is a dimensionless quantity used for characterizing the lattice ordering through statistical mapping of the two-dimensional radial distribution [116]. The rightmost column in Figure 10.8 shows the PCF for the corresponding perfect and imperfect crystals. The common x-axis of the plots is the distance normalized by the hole diameter \( D \). The black vertical lines depict the PCF of an ideal hexagonal lattice of infinite size. Because of the finite size of the actual samples, the peaks in the calculated PCF are not ideal delta functions but have a small spread. The position of the first peak signifies the mean center-to-center distance between the adjacent holes averaged over the entire imaged area. For all the three samples, the first peak occurs at 1.6 times the hole diameter, equal to 400
μm, the ideal lattice parameter. However, the PCFs of samples with lattice disorder display peaks of reduced heights and substantial broadening, indicative of the disruption of long-range lattice periodicity.

Figure 10.8 Top-view images of photonic crystal slabs with disorder in the lattice parameter. The holes have a diameter of 250 μm, and the lattice parameter of the nominally perfect sample is 400 μm. (a) Sample with no disorder in the lattice parameter. The first column shows a sample region within a 7 mm circular area. The second column shows a magnified portion of the image in the first column. The last column shows the pair correlation function (red) computed from the image in the first column. The (black) vertical lines depict the pair correlation function of a perfect lattice of infinite size. (b) Same as (a), but for a sample with slight disorder in the lattice parameter. (c) Same as (b), but with a greater degree of disorder in the lattice parameter. All scale bars in the first column are 1.5 mm, while those in the second column are 300 μm.

Figure 10.9 shows the transmission spectra of the samples shown in Figure 10.8. The transmission coefficient is plotted on a logarithmic scale to emphasize the differences between the spectra of the three samples. The transmission spectrum of the nominally perfect sample is shown in Figure 10.9(a), and contains several sharp resonant
features between 0.4 and 0.85 THz. Due to disorder in the lattice parameter, most of the resonant features in the spectra of the imperfect crystals are either completely washed out or substantially suppressed [Figures 10.9(b) & 10.9(c)]. For the imperfect crystal with lesser degree of disorder, very broadened yet still noticeable resonant dips are observed at around 0.6, 0.7, and 0.8 THz [Figure 10.9(b)]. This is because the perfect crystal has several resonances cluttered around these frequencies. As these collections of resonances broaden and overlap each other, the result is the observed small signatures. However, as the translational symmetry is further destroyed, the resonances are broadened even further [Figure 10.9(c)]. These results indicate that the guided resonances are very sensitive to disorder in the lattice parameter, and can be completely washed out with a disruption of the lattice periodicity.

![Figure 10.9 Normal-incidence transmission spectra of photonic crystal slabs with $r = 125 \mu m$, $a = 400 \mu m$, and $t = 300 \mu m$. (a) A perfect sample with no disorder in the lattice parameter [shown in Figure 10.8(a)]. (b) A sample with slight disorder in the lattice parameter [shown in Figure 10.8(b)]. (c) A sample with greater degree of disorder in the lattice parameter [shown in Figure 10.8(c)]]
10.5 Conclusion

We have studied the effect of lattice disorder on guided resonances in terahertz photonic crystal slabs with a hexagonal lattice of air holes in silicon. The normal-incidence transmission spectrum is obtained using terahertz time-domain spectroscopy. Moderate amounts of disorder in the hole shape and size does not appear to affect the lifetime of guided resonance modes significantly. On the other hand, the introduction of disorder in the lattice parameter severely broadens the resonant features in the spectrum. These results illustrate the extreme sensitivity of the guided resonance modes to lattice periodicity. Evidently, these modes are very cooperative in nature, with a high degree of spatial coherence extending over many lattice sites of the photonic crystal slab.
Chapter 11

Summary of results and future directions

The previous chapters present the analysis of two- and three-dimensional photonic crystals at different frequency regimes. All the results are summarized in this chapter. Finally, ideas for further research are proposed.

11.1 Summary of results

In recent years, photonic crystals have emerged as the most promising materials for the development of novel optical structures. In the previous chapters, fabrication, characterization, and numerical modeling of photonic crystals at three different frequency regimes, – x-ray, visible, and terahertz –, are discussed.

Fabrication of three-dimensional photonic crystals at x-ray wavelengths is extremely difficult because of the small sizes involved. Naturally occurring structures and biological organisms can provide a scaffold for realization of three-dimensional crystals with very small dimensions. Cowpea Mosaic Virus (CPMV), a plant virus, was exploited as a template for fabrication of patterned nanostructures with three-dimensional morphology. The crystals of the CPMV were infused with metals to fabricate optical materials of biological origin. These crystals have long-range order with nanometer scale detail, and are therefore three-dimensional photonic crystals capable of manipulating x-ray propagation. Calculations based on the transfer matrix method predict that these metal-infused crystals exhibit a normal-incidence reflectivity of 7% for wavelengths
around 35 nm, which can be utilized for soft x-ray optical systems. The results are explained in detail in Chapter 7.

Because the wavelength of visible light is larger than the x-rays, photonic crystals in the visible frequency range have larger feature sizes, and are easier to fabricate than the photonic crystals at x-ray frequencies. But the three-dimensional ordering requires expensive and cumbersome instrumentation. Consequently, self-assembly methods have become very popular for fabrication of colloidal crystals. This technique is described in Chapter 2. Chapters 3 to 6 describe the studies that were done on colloidal crystals. A theoretical study of superprism effect is presented in Chapter 3. This peculiar effect can be utilized to design various devices, including a novel sensor that is proposed in Chapter 4. However, because of a very narrow design window that is available for high resolution performance of the photonic crystal superprism, and due to the non-availability of perfect colloidal crystals, this property could not be observed experimentally (Chapter 5). Chapter 6 describes a new spin-coating technique that produces colloidal photonic crystals with a non-close-packed non-FCC lattice structure. Spectroscopic and microscopic studies, together with calculations, suggest that the colloidal particles form a non-close-packed hexagonal ABAB... type of lattice. This unconventional non-FCC lattice should enhance the functionality of the colloidal photonic crystals and could be useful for applications that require a highly porous lattice.

One of the reasons for the unsatisfactory superprism experiment (Chapter 5) was the non-perfect quality of the colloidal photonic crystals. THz photonic crystals can be fabricated with essentially zero structural disorder, and therefore, are promising candidates for studying the superprism effect. With this motivation, the superprism effect
was studied in a THz photonic crystal slab. A strong angular dispersion, characteristic of the superprism effect, was observed and analyzed (Chapter 8). Various THz photonic crystal slabs were also designed for the study of guided resonances (Appendix A). Chapter 9 describes the dependence of guided resonances on the structural parameters of the photonic crystal slab. Studies on the effect of structural disorder on the guided resonances are presented in Chapter 10. It was found that while the resonances are very tolerant to disorder in the hole radii, they are very sensitive to disorder in the lattice periodicity.

11.2 Future directions

To utilize the peculiar optical properties of photonic crystals for various applications, photonic crystals with good structural order are required. The THz regime has become an important area for the photonic crystal research, as the standard microfabrication techniques allow for the fabrication of essentially perfect THz photonic crystals. Most of the THz applications are based on free-space devices. There are very few demonstrations of photonic crystal devices at THz frequencies [285, 286]. Waveguide structures and associated devices like channel drop filters provide a model for studying the characteristics of photonic crystal devices in the THz regime. Realization of these devices will greatly contribute towards the development of THz photonics technology.

Based on the properties of THz photonic crystal slabs with hexagonal and square lattices, waveguides and channel drop filters were designed. These designs and their
expected performances are discussed in Section 11.3.

The fabricated THz photonic crystal slabs can also be used for other types of experiments. The studies on guided resonances presented in Chapters 9 and 10 are not only for normal-incidence, but also for the far-field. That is, the THz radiation was detected at distances far away (> 10 cm) from the crystal boundary. Similar experiments can be performed for the near-field. The electric field in the vicinity of the photonic crystal (< 500 μm) could be different than that in the far-field, and may allow for systematic study of Fano resonances in the near-field. More detail on this proposed experiment is described in Section 11.4.

The results obtained from the experiments described in Chapter 9 also contain information about the spectral phase. Therefore, the group velocity of the propagating pulse can be calculated from the measured phase difference. As discussed in Section 11.5, further analysis of the measured phase difference could reveal the cause of anomalous group velocity effects that were observed earlier [287].

11.3 Photonic crystal device structures at THz frequencies

Photonic crystal slabs are structures that have in-plane two-dimensional periodicity, and use index guiding to confine light in the third dimension [213]. Fabrication of THz photonic crystal slabs is described in Appendix A.

Waveguides are essential optical components for transferring light from one point to another. Conventional waveguides operate by index confinement, using the principle of total internal reflection. They do not exhibit any photonic band gap, and therefore,
suffer from radiation losses at sharp bends and corners [288]. A waveguide incorporated in a photonic crystal slab guides light in the plane by using photonic band gap properties. If the input frequency that is introduced into the waveguide falls within the photonic band gap, it cannot escape into the crystal and is guided along the waveguide [9]. Consequently, waveguides that use photonic crystal confinement in two dimensions and index guiding in the third, offer improved performance. In an air-hole photonic crystal slab, removing a row of holes or changing the hole radii creates a waveguide [223]. Rows of holes can be removed in a desired fashion, as shown in Figure 11.1 below.

![Figure 11.1](image)

**Figure 11.1** SEM pictures (top view) of photonic crystal slab waveguides. Left: A linear waveguide is created by removing a row of holes in a linear fashion. Right: Three linear waveguides are arranged to create a S-shaped waveguide, which consists of two 60° bends (the linear waveguide in the middle makes an angle of 60° with respect to the other two linear waveguides). The hole radius is 410 nm. Images taken from Reference [13].

A channel drop filter is used for wavelength division multiplexing [289]. It consists of waveguides coupled to a resonator. Depending on the properties of the waveguides, and the coupling efficiency between the waveguides and the resonator, specific frequencies can be channeled along desired directions, as shown in Figure 11.2.

To design a photonic crystal slab waveguide, calculation of the photonic band structure is required. From the band structure, the band gap range can be extracted. Using
this band gap range and the desired frequency of operation, the design parameters for the
photonic crystal slab can be determined. Channel drop filters in photonic crystals are based on waveguide structures, and can be designed from the same.

![Figure 11.2 Schematic of a channel drop filter [17]. Depending on the coupling between the bus and the drop waveguides, and the optical resonator system, any particular input frequency (f_i in the figure) can be channeled along a desired direction (forward: solid, backward: dashed).](image)

11.3.1 THz photonic crystal slab waveguide in a hexagonal lattice

In all the proposed designs, the photonic crystal slabs consist of an array of holes etched in silicon. Air holes are arranged in a hexagonal lattice and the refractive index of silicon is assumed to be 3.418. Two-dimensional band structure calculations [48] show that there is no complete band gap for $r/a=0.40$, and a decent complete band gap exists only for $r/a \geq 0.45$ (Figure 11.3). Here ‘r’ is the hole radius and ‘a’ is the lattice parameter. A two-dimensional band structure is applicable for designing a photonic crystal slab waveguide. This is because the band gap range for the photonic crystal slab differs from that of the two-dimensional structure by a very small amount [83, 210, 213].

For a purely TEM mode propagation, the waveguides should be operational below
0.5 THz (Figure 8.2). Table 11-1 shows the band gap range for two different values of \( r/a \), 0.45 and 0.475. Using this band gap range, corresponding design parameters for mid-gap frequencies of 0.25, 0.30, 0.35, and 0.40 THz are calculated. As the signal to noise ratio for the available spectrometers is highest around 0.3 THz, it is desirable to choose the design parameters such that the mid-gap frequency is around that value.

![Graphs showing the band structure for \( r/a = 0.45 \) and \( r/a = 0.475 \).](image)

**Figure 11.3** Two-dimensional band structure (first 5 bands, TM mode) of a photonic crystal with hexagonally arranged air holes in silicon, for \( r/a = 0.45 \) (left) and 0.475 (right). Yellow regions are complete photonic band gaps.

A waveguide can be created in a photonic crystal slab by removing a row of holes. The holes can be removed in any desired shape, depending on the application. Two-dimensional FDTD calculations [70] can be performed to evaluate the performance of the waveguide structures. One such calculation is illustrated in Figure 11.4, which shows the electric field distribution in a Y-shaped waveguide at the mid-gap frequency of 0.3 THz. The hexagonal lattice waveguide structures that were finally designed for further experiments are mentioned in Table A-2 (Appendix A).
<table>
<thead>
<tr>
<th></th>
<th>( r/a = 0.45 )</th>
<th>( r/a = 0.475 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete band gap range (a/( \lambda ))</td>
<td>0.4066 – 0.4439</td>
<td>0.4417 – 0.5114</td>
</tr>
<tr>
<td>Mid-gap frequency (a/( \lambda ))</td>
<td>0.4253</td>
<td>0.4765</td>
</tr>
<tr>
<td>Gap width/mid-gap (%)</td>
<td>8.8</td>
<td>14.6</td>
</tr>
<tr>
<td>Parameters in ( \mu m ) (for mid-gap=0.25 THz, or ( \lambda )=1200 ( \mu m ))</td>
<td>( r = 229.66 )</td>
<td>( r = 271.61 )</td>
</tr>
<tr>
<td></td>
<td>( a = 510.36 )</td>
<td>( a = 571.8 )</td>
</tr>
<tr>
<td>Parameters in ( \mu m ) (for mid-gap=0.30 THz, or ( \lambda )=1000 ( \mu m ))</td>
<td>( r = 191.38 )</td>
<td>( r = 226.33 )</td>
</tr>
<tr>
<td></td>
<td>( a = 425.3 )</td>
<td>( a = 476.5 )</td>
</tr>
<tr>
<td>Parameters in ( \mu m ) (for mid-gap=0.35 THz, or ( \lambda )=857.14 ( \mu m ))</td>
<td>( r = 164.04 )</td>
<td>( r = 194.00 )</td>
</tr>
<tr>
<td></td>
<td>( a = 364.54 )</td>
<td>( a = 408.43 )</td>
</tr>
<tr>
<td>Parameters in ( \mu m ) (for mid-gap=0.40 THz, or ( \lambda )=750 ( \mu m ))</td>
<td>( r = 143.54 )</td>
<td>( r = 169.75 )</td>
</tr>
<tr>
<td></td>
<td>( a = 318.97 )</td>
<td>( a = 357.37 )</td>
</tr>
</tbody>
</table>

Table 11-1 Design parameters for THz photonic crystal waveguides, calculated using the information from Figure 11.3.

Figure 11.4 FDTD calculation of the steady-state electric field distribution in a Y-shaped waveguide at 0.3 THz. The crystal parameters are: \( r=191.25 \) \( \mu m \), and \( a=425 \) \( \mu m \) \( \sqrt{r/a}=0.45 \). As 0.3 THz is the mid-gap frequency for the chosen design, the electric filed is confined in the waveguide region only.
11.3.2 THz photonic crystal slab waveguide in a square lattice

THz waveguides are also designed in photonic crystals slabs with square lattice of air holes in silicon. Similar to the hexagonal lattice, two-dimensional band structure calculations show that there is no complete band gap for r/a=0.40, and a decent complete band gap exists only for r/a ≥ 0.45 (Figure 11.5). Table 11-2 shows the band gap range for two different values of r/a, 0.45 and 0.475. Using this band gap range, corresponding design parameters for mid-gap frequencies of 0.25, 0.30, 0.35, and 0.40 THz are calculated.

![Graphs showing band structure](image)

**Figure 11.5** Two-dimensional band structure (first 5 bands, TM mode) of a photonic crystal with square lattice of air holes in silicon, for r/a=0.45 (left) and 0.475 (right). Yellow regions are complete photonic band gaps.

Two-dimensional FDTD calculations confirm the designs that are derived from the band structure. Figure 11.6 shows the electric field distribution in a 90°-bend waveguide at the mid-gap frequency of 0.35 THz. The square lattice waveguide structures that were finally designed for further experiments are mentioned in Table A-2 (Appendix A).
<table>
<thead>
<tr>
<th></th>
<th>(r/a = 0.45)</th>
<th>(r/a = 0.475)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete band gap range ((a/\lambda))</td>
<td>0.232 – 0.262</td>
<td>0.241 – 0.295</td>
</tr>
<tr>
<td>Mid-gap frequency ((a/\lambda))</td>
<td>0.2471</td>
<td>0.2679</td>
</tr>
<tr>
<td>Gap width/mid-gap (%)</td>
<td>12.2</td>
<td>20.0</td>
</tr>
<tr>
<td>Parameters in (\mu m) (for mid-gap= 0.25 THz, or (\lambda=1200 \mu m))</td>
<td>(r = 133.41)</td>
<td>(r = 152.73)</td>
</tr>
<tr>
<td></td>
<td>(a = 296.47)</td>
<td>(a = 321.54)</td>
</tr>
<tr>
<td>Parameters in (\mu m) (for mid-gap= 0.30 THz, or (\lambda=1000 \mu m))</td>
<td>(r = 111.17)</td>
<td>(r = 127.28)</td>
</tr>
<tr>
<td></td>
<td>(a = 247.06)</td>
<td>(a = 267.95)</td>
</tr>
<tr>
<td>Parameters in (\mu m) (for mid-gap= 0.35 THz, or (\lambda=857.14 \mu m))</td>
<td>(r = 95.29)</td>
<td>(r = 109.09)</td>
</tr>
<tr>
<td></td>
<td>(a = 211.76)</td>
<td>(a = 229.67)</td>
</tr>
<tr>
<td>Parameters in (\mu m) (for mid-gap= 0.40 THz, or (\lambda=750 \mu m))</td>
<td>(r = 83.38)</td>
<td>(r = 95.46)</td>
</tr>
</tbody>
</table>
|                             | \(a = 185.29\)  | \(a = 200.96\)  |}

Table 11-2  Design parameters for THz photonic crystal waveguides, calculated using the information from Figure 11.5.

Figure 11.6  FDTD calculation of the steady-state electric field distribution in a 90°-bend waveguide at 0.35 THz. The crystal parameters are: \(r=95.4 \mu m\), and \(a=212 \mu m\) \((r/a=0.45)\). As 0.35 THz is the mid-gap frequency for the chosen design, the electric filed is confined in the waveguide region only.
11.3.3 Channel drop filter at THz frequencies

Channel drop filters are waveguide structures with specifically tailored characteristics. They consist of waveguides coupled to an optical resonator. Waveguides support certain modes, which are transferred from or into them through the optical resonator(s) that are coupled to them. Figure 11.7 (rightmost picture) shows a channel drop filter based on a waveguide structure.

Figure 11.7 Device structures (top view) based on photonic crystal slabs with hexagonal lattice of air holes. Left: A perfect crystal. Middle: Air holes are removed from the perfect crystal to form waveguides along the linear direction (brown arrow) and along an angle of 60° (blue arrow). This device is same as sample #13 in Table A-2 (Appendix A). Right: A channel drop filter based on the device in the middle picture, same as sample #14 in Table A-2 (Appendix A). Expected functionality of this device is described in the text.

The middle picture in Figure 11.7 is the waveguide structure similar to sample #13 in Table A-2 (Appendix A). This device has parameters $r = 180 \, \mu m$ and $a = 400 \, \mu m$ ($r/a=0.45$), and therefore, has a band gap range of 0.305 - 0.333 THz. Consequently, the linear and 60°-bend waveguides support these frequencies along their path, with an expected transmission peak at the mid-gap frequency of 0.319 THz.

The channel drop filter (rightmost picture in Figure 11.7) utilizes the properties of this waveguide structure (sample #13), and is the same as sample #14 in Table A-2.
(Appendix A). Except that two optical resonators are placed in this waveguide structure: the first one is an air hole with $r/a = 0.34$ (red circle) placed in the linear direction, and the second one is an air hole with $r/a = 0.38$ (green circle) placed in the 60° direction. From the FDTD pictures like those in Figures 11.4 and 11.6, it was found that the air holes with $r/a = 0.34$ and $r/a = 0.38$ exhibit resonances at 0.313 THz and 0.324 THz, respectively. Because of the presence of these optical resonators, the corresponding resonant frequencies will couple selectively along the respective directions. In the region depicted by the black arrow, frequencies between 0.305 and 0.333 THz will be supported. The output along the 60° direction is expected to exhibit a transmission peak at around 0.324 THz, as the air hole with $r/a = 0.38$ (green circle) has a resonance at 0.324 THz. Similarly, the transmission along the linear direction is expected to exhibit a peak at around 0.313 THz, because of the resonance properties of the air hole with $r/a = 0.34$ (red circle).

11.4 THz near-field experiment

Chapters 9 and 10 present the analysis of guided resonances in photonic crystal slabs. In the band structure, the photonic crystal modes that lie above the light line can couple to the external radiation with various decay rates [228, 256, 290]. These leaky modes, called guided resonances, then interfere with the Fabry-Perot modes of the crystal to produce sharp resonant features in the normal-incidence transmission spectrum [230]. This phenomenon is analogous to that of the Fano resonances [230, 260].

The studies on guided resonances presented in Chapters 9 and 10 are for the far-
field. That is, the THz radiation was detected at distances far away (> 10 cm) from the crystal boundary. Similar experiments can be performed for the near-field. The electric field in the vicinity of the photonic crystal (< 500 μm) could be different than that in the far-field, and may allow for systematic study of Fano resonances in the near-field. A scanning near-field microscope is required for such measurements. Figure 11.8 shows the schematic of the experimental setup.

![Figure 11.8 Schematic of the scanning near-field microscopy experiment (by courtesy of Dr. Aurele Adam, Technical University Delft, Netherlands). The photonic crystal is placed on top of the electro-optic detector (GaP crystal). The microscope objective, which focuses the probe beam on to the electro-optic detector, scans small areas near the photonic crystal boundary.](image)

The scanning near-field microscope can be programmed to scan small areas just outside the photonic crystal boundary. The electric field distribution over the scanned region can be measured by an electro-optic detector (GaP crystal). Near-field measurements were performed on one of the photonic crystal slabs at Technical
University Delft, Netherlands. Typical scans covered an area of 1000 μm by 1000 μm, with a spatial resolution of 20 μm. Figure 11.9 (left) shows one such scan, together with the corresponding simulation result (right), at a frequency of 0.6 THz. Figures like these were generated for the entire frequency range of interest (0-2 THz), with a resolution of 6.5 GHz. Because of the limits of the available computational resources, the corresponding FEM calculations [73] were performed up to a frequency of 0.7 THz only. But the photonic crystal slab exhibits two resonant features present below 0.7 THz in the far-field spectrum [246], and a comparison in the near-field is still possible.

![0.6 THz](image_url)

*Figure 11.9 Electric field distributions just outside the photonic crystal boundary, over an area of 1000 μm by 1000 μm. Left: Measured field at 0.6 THz, obtained by scanning near-field microscope. Right: The corresponding calculations performed using finite elements method (right). The experimental results match well with the FEM calculations. The crystal parameters are r = 180 μm, a = 400 μm, and slab thickness t = 305 μm.*

The near-field spectra were compared with the far-field data. However, the resonant features did not appear much different. In Figure 11.8, the photonic crystal is shown to be placed on top of the GaP detector, meaning that the field was measured at a distance of 0 μm (or almost zero μm) from the crystal boundary. Measurements were also
made for non-zero distances (ranging from 0 to 2000 μm) between the photonic crystal and the GaP detector. The near-field spectra still did not show any changes.

The same experiment can be performed on crystals with deliberately introduced lattice disorder (samples #7 and #8, in Table A-1, Appendix A). The resonant features in the near-field may be different from those in the far-field due to the introduced lattice disorder. A systematic study would then provide a better explanation of Fano resonance in the near-field.

11.5 Anomalous group velocity effects

The results obtained from the experiments described in Chapter 9 also contain information about the spectral phase. Therefore, the group velocity of the propagating pulse can be calculated from the measured phase difference. The group velocity \( v_g \) can be calculated from the measured phase difference using the standard formula:

\[
\frac{v_g(\omega)}{c} = \left[ 1 + \frac{c}{L} \frac{d(\Delta \psi)}{d\omega} \right]^{-1}
\]  

(11.1)

Here \( c \) is the speed of light in vacuum, and \( \Delta \psi \) is the phase difference produced when light travels a distance \( L \) in the given medium. The phase difference \( \Delta \psi \) is generally a smoothly varying function of the frequency, and accounts for the group delay for propagation of light through a medium. However, if the measured phase difference is independent of the frequency, then the group velocity is equal to the speed of light in vacuum.

A quick analysis of the measured phase difference for the various samples studied in Chapter 9 revealed that as the volume occupied by the holes become greater than 50%,
the phase difference becomes independent of the frequency in the range 0.9 – 1.5 THz. This means that for samples with hole volume fraction greater than 50%, there is no group delay in the frequency range 0.9 – 1.5 THz, and light travels as if there was no slab present.

At this point, it is not clear why there is no group delay for samples with hole volume fraction greater than 50%. It is worth mentioning that this bizarre result is not a function of the hole size, but the hole volume fraction (or the r/a ratio). This is because samples with same hole radii but different r/a value exhibit different properties with respect to the spectral phase. Further analysis of the pulse envelope may provide some insight into the mechanism of this unusual property.

11.5 Conclusion

In conclusion, the fabricated terahertz photonic crystals can be utilized for studies like the near-field measurements and the anomalous group velocity effects. The proposed designs also promise realization of waveguide structures and channel drop filters based on terahertz photonic crystal slabs.
Bibliography


Appendix A

Fabrication of terahertz photonic crystals by photolithography

This appendix describes the procedure that was employed to fabricate terahertz photonic crystals. The entire process of mask fabrication and photolithography are explained in detail.

A.1 Photonic crystal parameters

Photonic crystals active in the terahertz (THz) range of frequencies can be fabricated with essentially zero structural disorder. This is because the size of the device features is in the order of several microns, and can be easily obtained by conventional microfabrication techniques. THz photonic crystal slabs were designed for studying various waveguide structures, as well as for analyzing guided resonances (described in Chapters 9 and 10). The samples consist of circular holes etched all the way through a high-resistivity silicon slab. Waveguide samples consist of rows of missing holes, in linear, T, and Y shapes. Two parameters were required for designing the appropriate samples: radius ‘r’ of the holes, and the lattice parameter ‘a’ – the center-to-center distance between the holes.

The following two tables specify the design parameters of the various samples. The holes are arranged in either hexagonal or square lattice. Random1 and Random2 in Table A-1 refer to hexagonal lattices with different degrees of disorder introduced into them (see Chapter 10 for more information). The right most columns in the two tables depict the name of the CAD file corresponding to each sample. These CAD files are in
dxr format and were created using RSoft® CAD Tool. CAD files with dxf format can also be created using AutoCAD®. However, the RSoft CAD Tool seems more convenient. The CAD files are saved in the CD accompanying this thesis.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Lattice type</th>
<th>r (μm)</th>
<th>a (μm)</th>
<th>Thickness (μm)</th>
<th>r/a</th>
<th>CAD file name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexagonal</td>
<td>150</td>
<td>400</td>
<td>250</td>
<td>0.375</td>
<td>Hr150a400.dxf</td>
</tr>
<tr>
<td>2</td>
<td>Hexagonal</td>
<td>150</td>
<td>400</td>
<td>275</td>
<td>0.375</td>
<td>Hr150a400.dxf</td>
</tr>
<tr>
<td>3</td>
<td>Hexagonal</td>
<td>150</td>
<td>400</td>
<td>300</td>
<td>0.375</td>
<td>Hr150a400.dxf</td>
</tr>
<tr>
<td>4</td>
<td>Hexagonal</td>
<td>125</td>
<td>400</td>
<td>300</td>
<td>0.3125</td>
<td>Hr125a400.dxf</td>
</tr>
<tr>
<td>5</td>
<td>Hexagonal</td>
<td>150</td>
<td>480</td>
<td>300</td>
<td>0.3125</td>
<td>Hr150a480.dxf</td>
</tr>
<tr>
<td>6</td>
<td>Hexagonal</td>
<td>150</td>
<td>575</td>
<td>300</td>
<td>0.26</td>
<td>Hr150a575.dxf</td>
</tr>
<tr>
<td>7</td>
<td>Random1</td>
<td>125</td>
<td>400</td>
<td>300</td>
<td>0.3125</td>
<td>Rr125a400d125.dxf</td>
</tr>
<tr>
<td>8</td>
<td>Random2</td>
<td>125</td>
<td>400</td>
<td>300</td>
<td>0.3125</td>
<td>Rr125a400d200.dxf</td>
</tr>
<tr>
<td>9</td>
<td>Square</td>
<td>180</td>
<td>400</td>
<td>300</td>
<td>0.45</td>
<td>Sr180a400.dxf</td>
</tr>
<tr>
<td>10</td>
<td>Square</td>
<td>150</td>
<td>400</td>
<td>300</td>
<td>0.375</td>
<td>Sr150a400.dxf</td>
</tr>
</tbody>
</table>

Table A-1: Photonic crystal samples for the study of guided resonances at THz frequencies.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Lattice / waveguide</th>
<th>r (μm)</th>
<th>a (μm)</th>
<th>r/a</th>
<th>CAD file name</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Hexagonal / linear (L)</td>
<td>180</td>
<td>400</td>
<td>0.45</td>
<td>Hlinear.dxf</td>
</tr>
<tr>
<td>12</td>
<td>Hexagonal / 60° bend</td>
<td>180</td>
<td>400</td>
<td>0.45</td>
<td>Hsixty.dxf</td>
</tr>
<tr>
<td>13</td>
<td>Hexagonal / (L+ 60°)</td>
<td>180</td>
<td>400</td>
<td>0.45</td>
<td>Hlinsixty.dxf</td>
</tr>
<tr>
<td>14</td>
<td>Channel drop filter</td>
<td>180</td>
<td>400</td>
<td>0.45</td>
<td>Hcdf.dxf</td>
</tr>
<tr>
<td>15</td>
<td>Square (perfect)</td>
<td>112.5</td>
<td>250</td>
<td>0.45</td>
<td>Sperfect.dxf</td>
</tr>
<tr>
<td>16</td>
<td>Square / linear</td>
<td>112.5</td>
<td>250</td>
<td>0.45</td>
<td>Slinear.dxf</td>
</tr>
<tr>
<td>17</td>
<td>Square / 90° bend</td>
<td>112.5</td>
<td>250</td>
<td>0.45</td>
<td>Sninety.dxf</td>
</tr>
</tbody>
</table>

Table A-2: Various THz photonic crystal waveguide structures.
A.2 Mask fabrication

The CAD files are first converted into a machine readable format (lic) using an available conversion software (Convert8.6). The conversion software creates a folder with the same name as the dxf file. This folder contains all the appropriate lic files, and is transferred to the hard drive of the computer connected to the mask maker (Hiedelberg DWL66).

A mask of maximum size 4-inch by 4-inch can be created using the available mask maker. The samples on the mask should be within a 4-inch circular area. This is because the pattern on the mask will be finally transferred to a 4-inch silicon wafer. As each photonic crystal sample fits within an area of 2.25 cm by 2.25 cm, a maximum of seven samples can be accommodated on a 4-inch silicon wafer (Figure A.1). To arrange the samples on the mask as shown in Figure A.1, the following map is used:

<table>
<thead>
<tr>
<th>Field width</th>
<th>275000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field height</td>
<td>275000</td>
</tr>
<tr>
<td>Alignment X</td>
<td>0</td>
</tr>
<tr>
<td>Alignment Y</td>
<td>0</td>
</tr>
<tr>
<td>Fields per row</td>
<td>2, 3, 2</td>
</tr>
<tr>
<td>Field start at X</td>
<td>13750, 0, 13750</td>
</tr>
<tr>
<td>Field zero</td>
<td>4</td>
</tr>
</tbody>
</table>

The above map generates seven exposure fields on the mask, arranged in a fashion shown in Figure A.1. Each field has a size of 2.75 cm by 2.75 cm. Each field can be assigned a desired sample (folder name containing the lic files). Total time for writing
the samples on the mask depends on the number of samples being written (each sample takes about 5.25 hours).

![Diagram of 4-inch mask and wafer](image)

**Figure A.1** A total of seven samples are written on the 4-inch mask. The seven samples are arranged in such a way that they can be transferred to a 4-inch wafer. The green color depicts the area covered by the samples.

The mask consists of 530 nm thick layer of AZ1518 (positive photoresist) coated on a low-reflective chrome layer that is deposited on soda lime glass. After the desired pattern is written, the mask is developed for 2 minutes. The developing solution is prepared by mixing a standard positive photoresist developer (Microposit 351 or AZ Developer) and water in the ratio of 1:4 (40 ml : 160 ml). The exposed chrome is then etched by dipping the mask in the chrome etchant solution (40 ml of CEP-200 Microchrome) for 2 minutes. Finally, the remaining photoresist is stripped by a positive photoresist stripper (PRS-100) in about 5 minutes. During the processes of developing, etching, and stripping, it is important to mildly agitate the mask. After each step, the mask should be rinsed with DI water for about 2 minutes. A picture of the whole mask is shown in Figure A.2. Figure A.3 shows microscopic images of the samples written on the mask.
A total of 3 masks were fabricated. Two masks contained seven samples each. The seven samples in the first mask (Figure A.2) were samples numbers 3 – 9 from Table A-1. The second mask contained designs of sample numbers 11 – 17 (Table A-2). The third mask contained four identical samples: sample number 1 (or 2) from Table A-1.

Figure A.2 A 4-inch mask after it has been completely processed. Due to reflection from the mask, the sample features appear blurred in the photograph.

Figure A.3 Microscopic images of the samples written on the mask. Left: $r = 120\mu m$, $a = 300\mu m$. Right: $r = 240 \mu m$, $a = 500 \mu m$. The pink color depicts chrome, whereas the grayish color depicts the regions from where chrome has been etched out. Chrome can be etched out from the desired location (holes, or areas other than holes) by specifying the relevant exposure mode (inverted or non-inverted) while converting the dxf files into lcs format.
A.3 Photolithography steps

Figure A.4 shows the schematic of the whole lithography process. Gray, pink, and brown colors correspond to silicon, oxide (SiO$_2$), and photoresist, respectively. The orange color depicts the exposed photoresist. The pattern is first created on the sacrificial photoresist layer. After transferring the pattern from the photoresist layer to the oxide layer, the exposed silicon is etched to obtain the photonic crystal slab. The next sections explain each of the steps involved in the fabrication process.

Figure A.4 A schematic of the lithography process. Gray, pink, and brown colors correspond to silicon, oxide (SiO$_2$), and photoresist, respectively. The orange color depicts the exposed photoresist.
Silicon wafers with 1 µm thick thermal oxide layer were obtained from a vendor (SQI, Inc.). The wafers were cleaned by dipping them in piranha solution (H₂SO₄ and H₂O₂ in the ratio of 4:1) for about 30 minutes, followed by rinsing with DI water and blowing them dry with a stream of nitrogen. Finally, the wafers were baked at 110° C for 2 minutes.

A.3.1 Photoresist deposition

For optimum adhesion of the photoresist to the wafer surface, the wafer is first treated with MCC Primer (MicroChem). This solution is a mixture of 80% HMDS (hexamethyldisilazane) and 20% polymethyl acetate. A positive photoresist (S1813) is then spin-coated on the wafer surface. The steps are:

1) Pour 600 µL of MCC Primer on the clean wafer surface and wait till it covers the entire wafer surface.
2) Spin-coat at 4000 rpm for 30 seconds.
3) Bake the wafer at 110° C for 2 minutes.
4) Pour 1200 µL of S1813 on the wafer surface. Avoid air bubbles. Tilt and turn the wafer to make the solution cover the entire wafer surface.
5) Spin-coat at 4000 rpm for 30 seconds.
6) Bake the wafer at 110° C for 2 minutes.
A.3.2 Pattern exposure

After the photoresist has been deposited on the wafer surface, the pattern can be transferred from the mask to the photoresist layer by using a mask aligner and exposure tool (SUSS Mask Aligner MJB4). For exposing patterns on a 4-inch wafer, a 5-inch mask is required. Unfortunately, creating masks of size greater than 4-inch is not possible with the available mask maker. Below is the description of how a 4-inch mask was used to transfer patterns on a 4-inch wafer.

Figure A.5 shows the picture of the mask holder. A circular ring (1 mm wide, 1-2 mm deep) on the rear side of the holder serves the purpose of securing the mask when vacuum is generated inside the ring. The diameter of this circular ring (dashed circle in Figure A.5) is a larger than 4-inch. So a 4-inch mask will not cover the ring entirely, and hence, is a little small for this holder. A 5-inch mask will cover the ring entirely, and the vacuum inside the ring will make the mask stick to the holder perfectly.

![Figure A.5 Picture of the mask holder. Left: front side. Right: Rear side of the holder. A dashed curve is superimposed on the ring to emphasize its location.](image)

The only purpose of the holder is to hold the mask, and the vacuum in the ring ensures that the mask is properly secured and attached to the holder. In principle, a good
double-stick tape can be used to attach the mask to the holder just as well. However, just using a good double-stick tape is not enough. This is because the vacuum that is generated in the ring has to be turned on during the exposure cycles. The machine will show “vacuum error” if the ring is not entirely covered by the mask (as in the case of 4-inch mask). Therefore, a single-sided tape is stuck on top of the ring at all places. This eliminates the “vacuum error”. Then a double-stick tape is used at four corners to stick the mask to the holder.

![Alignment marks](image)

**Figure A.6** Picture of the rear side of the mask holder. The circular ring is covered with one-sided tape to eliminate the “vacuum error”. Double-sided tape is placed at locations marked 1, 2, 3, and 4. The alignment marks ensure that the patterns are exposed with respect to the wafer center.

Double-stick tape is stuck at locations marked 1, 2, 3 and 4 (Figure A.6). Just placing the mask on top of the double-stick tape and pressing it lightly secures the mask very well. The mask attaches to the holder just like it would have through the vacuum. Any kind of contact mode works perfectly (hard, soft, vacuum, etc.)

For this particular mask-aligner, alignment marks were made on the holder, signifying the location where the edges of the mask should be placed. This ensured that the center of the mask coincided with the center of the wafer during the exposure.
Once the mask was attached to the mask holder, the pattern was exposed on the photoresist-coated wafer. Soft-contact mode with an exposure time of 2 seconds was used. The next section describes how the wafer was processed to obtain the desired samples.

A.3.3 Wafer processing

The following procedure was carried out to process the wafers on which the patterns had been exposed:

1) Develop the wafer for 3 minutes. The developing solution was prepared by mixing positive photoresist developer (Microposit 351) and DI water in the ratio of 1:4. It is important to mildly agitate the wafer during the developing process, and also to rinse the wafer thoroughly with DI water after developing. An image of the developed sample is shown in Figure A.7(a).

2) Bake the wafer at 110° C for 10 minutes. This is done to ensure a better quality of the wet-etch process that follows. The wet-etch process should be started within 30 minutes after the wafer has been baked.

3) Etch the exposed oxide. This is best done by using a RIE (reactive-ion-etcher) machine. Because of non-availability of the RIE, the wafer was wet-etched. A BOE solution (buffered oxide etch) was prepared by adding 25 ml of 49% HF in a 40% NH₄F solution (50 g of NH₄F mixed in 75 ml DI water). As the oxide thickness is 1 μm, the wafer was dipped in the BOE for a little more than 10 minutes to ensure complete etching of all the exposed oxide (the BOE etch rate is
0.1 μm/min). It is very important to mildly agitate the solution during the etch process, and to rinse the wafer thoroughly with DI water after the etching. Figure A.7(b) shows an image of the sample after the exposed oxide has been etched.

4) Dissolve the photoresist. This is done by dipping the wafer in positive photoresist stripper (PRS-100) for 5 minutes. Figure A.7(c) shows an image of the sample.

![Figure A.7](image)

Figure A.7 Typical microscopic images of the sample during various stages of processing. Grayish, pink, and white colors depict photoresist, oxide, and silicon, respectively. Samples with different hole sizes are shown. (a) Picture of the wafer after the exposed photoresist has been developed to reveal the (pink) oxide underneath. (b) Picture of the wafer after the exposed oxide in (a) has been etched to reveal the (white) silicon underneath. (c) Picture of the wafer after the remaining photoresist in (b) has been dissolved to reveal the (pink) oxide underneath.

Besides visual observation, the quality of the final wafer (patterned oxide layer on top of silicon) can be checked by a profilometer. Figure A.8 shows the profilometer data that was obtained from a typical sample.

The profilometer data confirms that the oxide thickness is 1 μm (10,000 Angstroms). The steep variation in height signifies straight walls with no or minimal undercut. The figure also shows that the wafer thickness (for this particular wafer) varies by 1 μm (10,000 Angstroms) over a distance of 1 cm (10,000 μm). This was expected since the TTV (total thickness variation) of the wafers was ±2 μm (specified by the wafer vendor).
Figure A.8 Profilometer data obtained from a sample similar to the one shown in Figure A.7(c). The oxide thickness is 1 μm (10,000 Angstroms). The wafer thickness (for this particular wafer) varies by 1 μm (10,000 Angstroms) over a distance of 1 cm (10,000 μm). The steep variation in height signifies straight walls with no or minimal undercut.

A.3.4 Silicon etching by DRIE

The final step involves etching the exposed silicon windows to obtain the photonic crystal slab. As the thickness of the silicon wafers are in the range 250-300 μm, this can be accomplished only by DRIE (deep-reactive-ion-etching). Due to non-availability of the DRIE machine, the wafers (with patterned oxide layer) were sent to a vendor for processing (Blu-Si, Inc.).

A.4 Summary

To summarize, this appendix describes the procedure of mask fabrication and lithography for fabrication of THz photonic crystals. The information presented here could be useful to researchers working in the clean room at Rice University.
Appendix B

Numerical computation of the superprism effect

As mentioned in the last paragraph of Section 3.1, this appendix presents a tutorial on how to use the series of codes written in Scheme and Matlab for numerical computation of the superprism effect. The description provides details on how to obtain various results such as the complete photonic band structure, equal-energy surfaces, internal propagation directions, etcetera. Although these codes were used to calculate the superprism effect in inverted opals, they are applicable to any type of photonic crystals.

Though it is not necessary to follow the sequence in which the codes are described, it is evident from the methodology explained in Chapter 3 that certain order needs to be pursued. For example, it is obvious that the complete photonic band structure needs to be calculated for computation of the dispersion surface; and similarly, the internal propagation direction cannot be calculated unless the equal-energy surface has been constructed. However, there may be multiple codes for determining the same property and they can be used in any random order. Nevertheless, for accurate results it is advisable to follow the exact sequence in which the codes are described since some of the earlier codes optimize the data that is used by latter codes. All the codes and results are saved in the CD accompanying this thesis.

B.1 Photonic band structure calculation

All the codes for band structure calculations were written in scheme and were executed by a freely available software package that utilizes the plane wave method. This
software computes definite-frequency eigenstates of Maxwell’s equations in periodic
dielectric structures for arbitrary wave vectors, using fully-vectorial and three-
dimensional methods, and is specifically designed for the study of photonic crystals. One
can define a desired geometry as explained in the “user tutorial” of this software manual.
For better convergence of the photonic bands, a grid with appropriate mesh size is
required for discretization of the defined unit cell. The parameters which are usually
changed after writing the code are the ‘number of bands’ to be calculated, and the
‘dielectric constant’ of the individual structures comprising the unit cell geometry.

The first step is to calculate the standard photonic band structure. The next step is
calculation of the band structure from the center of the Brillouin zone (Γ point) to other
high symmetry points, and compare them to check the anisotropy of the bands. Finally,
complete band structure is computed for construction of dispersion surfaces.

B.1.1 Standard photonic band structure

The codes are executed by the freely available software MPB, which is installed
on a linux server ‘ece-76-51.ece.rice.edu’. The code for calculating the standard band
structure for the macroporous polymer photonic crystal is called cbs.ctl (scheme codes in
MPB have the extension ctl). As can be seen in the code, a grid of $16 \times 16 \times 16$ is used
with a mesh size of 7 for better convergence. To simulate the structure of macroporous
polymer templates, lattice geometry for the FCC lattice is defined and the ratio of sphere
radius to the primitive unit cell length is set to be slightly more than 0.5 ($r/a = 0.53$).
This corresponds to placing the air spheres slightly closer together than their diameters,
leading to small windows that interconnect the internal air network. This accurately
reproduces the morphology of the samples (see Chapter 3). The dielectric constant of the polymer background is defined as 2.5281 (corresponding to \( n_p = 1.59 \)), which is roughly the value for polystyrene. This code takes a few minutes to execute and an output file (cbs.out) is generated in the same directory. Required data (plotted in Figure 3.1) is extracted from the output file (using standard Linux commands given in software manual) and is saved in a data file (cbs.dat).

B.1.2 Nature of bands: isotropic and anisotropic

The directory SuperPrism/FCC/Bands has sub-directories ‘Gamma-K’, ‘Gamma-L’, ‘Gamma-U’, ‘Gamma-W’, ‘Gamma-X’ which have control files for calculating band structures from \( \Gamma \) point to other high symmetry points on the Brillouin zone surface: K, L, U, W, and X respectively. These control files are exactly same as cbs.ctl (mentioned in Section B.1.1) but with a slight difference: the band structure is calculated from \( \Gamma \) point to one of the high symmetry points only. Respective data files are used to depict the nature of bands, as shown in Figure 3.2.

B.1.3 Complete photonic band structure

For calculation of dispersion surfaces, a complete photonic band structure is needed. In other words, we must calculate the band structure from the \( \Gamma \) point to all possible points on the Brillouin zone surface, not merely to the high symmetry points. We can of course use the symmetry of the Brillouin zone to reduce the computational load. Figure B.1 shows the first Brillouin zone of the FCC lattice and the lines between the small white circles define the boundaries of the irreducible part of the zone. Because of
the Brillouin zone symmetry, one only needs to calculate the band structure from Γ point to all possible points on the surface of this irreducible part.

![Brillouin Zone Diagram](image)

**Figure B.1** First Brillouin zone of the face-centered-cubic (FCC) lattice. The lines between the small white circles define the boundaries of the irreducible part of the zone. Calculations done for this irreducible part can be extended to the whole Brillouin zone through symmetry operations.

As it can be seen from Figure B.1, the outer surface of the irreducible part can be divided into three triangular planes: K¸L¸W plane, L¸U,W plane and W¸U,X plane. Codes are written to calculate the complete band structure for these three planes (see the end of this Appendix) and then the results are combined to obtain the complete band structure for the irreducible part of the Brillouin zone. The directory `SuperPrism/FCC/DispersionSurface/PSdata` has three sub-directories named K¸L,W, L¸U,W and W¸U,X. Each contains control files that calculate the band structure from the Γ point to all possible points on the surface of the respective plane. The parameters and geometry used in all the control files are same as those used previously (as described in Section
B.1.1), except that lesser number of bands (four) are calculated (since superprism effect is calculated for the 4th or lower band). For example, one of the control files klwn1580.ctl (in folder K LW) calculates the photonic band structure from Γ point to all possible points on the surface of the K LW plane. The increment in k-point is of the order of 10⁻³ so that the whole surface of the respective plane can be accurately covered by all the generated k-points. ‘n1580’ part of the file name means that the calculation is done for a polymer background with a refractive index of 1.580, and this information is also documented in the code. Similar documentation is done for control files in folders LUW and WUX. For example, luwn15894.ctl (in folder LUW) and wuxn15912.ctl (in folder WUX) calculate the lowest 4 bands from Γ point to all possible points on the respective plane surface (LUW and WUX respectively), and the value of polymer refractive indices in these codes are 1.5894 and 1.5912 respectively. Corresponding output files and data files are saved in each folder. The combined data of all the three planes comprising the surface of the irreducible part is used for the calculation of dispersion surface or equal-energy surface, as described below.

B.2 Dispersion surface and propagation direction calculation

The complete photonic band structure gives information about how the band structure varies from Γ point to all possible points on the Brillouin zone surface. From this, all possible values of wave vectors in the three-dimensional space for a particular energy or frequency can be extracted. The plot of all these wave vectors in the k-space for a particular energy gives an equal-energy surface known as a dispersion surface. It is analogous to the index ellipsoid in conventional crystal optics or to the Fermi surface in
electronic crystals.

Codes for calculating dispersion surfaces and propagation directions are written in *matlab*, and are saved in the folder SuperPrism\Dsplots. In the subsequent sections, a tutorial on the capabilities of codes is presented. All the codes that are explained are saved in SuperPrism\Dsplots\d001, and they pertain to results of Chapters 3 and 4.

Wave vector value for a particular frequency is extracted from the band structure through interpolation. In *matlab*, the function from which data is extracted by interpolation needs to be monotonic. The bands calculated for lower frequencies are monotonic, and therefore, the complex situation of duplicate values of wave vector for single value of frequency does not arise. At higher frequencies, bands (5 or higher) are very non-monotonic and the analysis becomes complex. Although we are limited to calculation of superprism effect for the 4th or lower bands, which are essentially monotonic, the 4th band has some non-monotonic tendency at the end values since it sweeps the partial band gap edge. A code *monotonic.m* was written to detect the few values of frequency (generally the last value of the band) that were making the band structure non-monotonic. These values are replaced by NaNs (not a number) to make the band monotonic. The accuracy is not affected at all since only one value (the last) in some of the bands needed conversion to NaNs and these values differed from the immediate previous values by an order of $10^{-3}$.

In all the codes, the primary step is to load the appropriate data files that were generated by *scheme* programming (the nomenclature and documentation of these data files are explained in Section B.1.3). Next, two values need to be correctly entered: the frequency at which the dispersion surface is desired to be calculated, and the band in
which this particular value of frequency lies. The first few lines of all the codes are:

\[ \begin{align*}
  w &= 0.30; \quad \% \text{frequency (Be sure that this value lies in band 'b')} \\
  b &= 6; \quad \% \text{Band#4:b=9 Band#3:b=8 Band#2:b=7 Band#1:b=6} \\
  \text{incr} &= 0.0025; \quad \% \text{spacing between k-points in the dispersion surface}
\end{align*} \]

The first parameter (w) is the frequency and the value of ‘b’ selects the band in which ‘w’ lies. ‘incr’ is the increment in k-points which are used in constructing the dispersion surface. The less the value of ‘incr’, denser is the dispersion surface and more time it takes for the codes to execute. To get the desired result, the user needs to input the required value of ‘w’ and ‘b’. For example, if one wants to calculate the dispersion surface at a frequency value of 0.73, then the respective ‘w’ and ‘b’ values would be 0.73 and 9 (since this frequency value lies in band 4). The user would only need to change these values in the code to get the desired result (assuming that the appropriate data files are being loaded, of course).

A series of codes were written for analyzing the superprism effect with respect to the \{111\} set of planes since they are most readily accessible experimentally. A few results for the \{001\} face were also calculated since it is possible to grow the colloidal crystals with this face exposed by employing specially patterned surfaces. There is extensive documentation within the codes and every set of programming commands are accompanied by comprehensive remarks to make the scripts lucid and easy to modify. The following sections present a step-by-step approach for calculation of dispersion surfaces and propagation directions for specific set of planes.
B.2.1 Calculation with respect to \( \{001\} \) set of planes

There are a total of eleven codes that are used to produce the desired results. They generate a plot with respect to [001], [010], [100] set of orthogonal triplet (all results are with respect to \( \{001\} \) set of planes, numerically as well as visually). As mentioned before, documentation within the codes is very extensive and the codes are self-explanatory. Hence minimum explanation is presented here.

1) ds001fnc.m: This code (see the end of this Appendix) generates the full dispersion surface and plots it inside the first Brillouin zone (Figure 3.3). First, all possible values of wave vectors in the three-dimensional space for a particular frequency are extracted from the complete band structure of the irreducible part of the Brillouin zone. Then these wave vector values are replicated in accordance with the symmetry exhibited by the Brillouin zone to produce wave vectors corresponding to the whole Brillouin zone surface. The code generates and plots a surface grid after every replication, and hence the plot is referred to be consisting of ‘non-continuous’ data. By this terminology, if the surface grids were generated using all the replicated data collectively, then the plot would consist of ‘continuous data’. The plot of all these wave vectors in the k-space for a particular frequency gives the equal-energy surface or the dispersion surface. The user needs to input the frequency ‘\( w \)’ at which the dispersion surface is desired and the band ‘\( b \)’ in which this frequency lies; and of course, make sure that the appropriate data files are being loaded.

2) ds001pnc1.m: This code is same as 1) above, but the dispersion surface is generated in
one octant only. This is because the results in one octant can be replicated for other octants due to symmetry properties. Since data for only one octant is generated, the number of times the primary data is replicated is lesser, shortening the computational time significantly. Non-continuous data is used for plotting.

3) ds001pnc2.m: Same as 2) above with the addition that propagation wave vectors and directions are plotted. It gives an idea about the beam orientation and confinement within the photonic crystal. Besides generating propagation direction of the beam for different input orientations, the code produces a plot to depict them visually, as shown in Figure B.2. Since there can be numerical errors due to low density of surface grids, the basic use of this code is to visually check for deviant behavior, if any, and estimate and improve its resolution and accuracy. The results may or may not be accurate.

![Figure B.2 Plot generated by ds001pnc2.m matlab code. Dispersion surface (brown) is generated in one octant only. Propagation wave vectors (red, from the $\Gamma$ point to the dispersion surface) and propagation directions (blue, gradients at the end point of the propagation wave vectors) are plotted. Since the view is from outer face of the dispersion surface, propagation wave vectors are not seen, but red spots on dispersion surface depicts the end points of those vectors. For this particular plot, all gradients lie in one plane, which means that the beam propagation is confined in one plane (in-plane propagation).](image-url)
4) \texttt{ds001pc1.m}: Same as 2) above but with the difference that continuous data is used.

5) \texttt{ds001pc2.m}: Same as 3) above but with the difference that continuous data is used. The plot is shown in Figure B.3. It can be easily inferred that although the surface is depicted in a much better way in case of non-continuous data, the continuous data covers a broader range of the generated propagation directions due to smoothness at the curvature. Nevertheless, there are gaps in the range of generated propagation directions for both continuous and non-continuous data, implying the need for denser surface grids for better accuracy.

![Figure B.3](image.png)

\textbf{Figure B.3} Same as Figure B.2 but with continuous data being used in calculation (\texttt{ds001pc2.m}). Since the view is from a different angle, propagation wave vectors (red) are visible too.

6) \texttt{normc.m}: This code uses the data generated from 2) above, and draws the propagation wave vector and the propagation direction for a particular incident orientation. \texttt{ds001pnc1.m} needs to be executed before running this code. One of the plots generated
using *ds001pnc1.m* and *normc.m* is shown in Figure 3.10 of Chapter 3. For appropriate display and plot, the incident orientation in *normc.m* should be within the defined octant in *ds001pnc1.m*.

7) *ds001tpvlti.m*: This code calculates the relation between $\theta_p$ and $\theta_{in}$ with respect to the normal of \{001\} face. The incident orientation is chosen in a way such that the beam is confined in one plane and its propagation can be parameterized by a single angle. Continuous data and denser grid size is used, and the incident and propagation angle values are displayed in the command window during execution. The data is also saved in a file for plotting outside *matlab*. The data generated by this code is plotted in Figure 3.6 of Chapter 3.

8) *ds001phd.m*: This code generates a very small portion of the dispersion surface. This small portion of the dispersion surface (around a point governed by the incident angle) has a very high density of grid points (increment in k points is 0.0002) and hence highest possible accuracy (within numerical limits) in the calculation of internal propagation angles. Continuous data is used to preserve the smoothness in curvature, which eliminates deviant behavior. The plot generated by this code is shown in Figure B.4. The values of incident and propagation angles are displayed in the command window during execution. This code is useful for calculating the variation in the propagation direction as a function of frequency, for a fixed incident orientation of the light beam. The basic use is to check the accuracy (both numerically and visually) and to develop a similar code to calculate the whole range of propagation directions in a precise way.
Figure B.4 Small portion of the dispersion surface generated using ds001phd.m matlab code. This small portion of the dispersion surface has very high density of grid points for highest possible accuracy. Red line is the propagation wave vector and the blue line is the propagation direction.

9) ds001tpvw1.m: Using 8) above as template, this code calculates the relation between $\theta_p$ and frequency for a fixed incident orientation. Since the incident orientation is such that the beam is confined in a plane ($\phi_{in} = \phi_p$), propagation direction can be parameterized by a single angle. Values are with respect to {001} face.

10) ds001tpvw2.m: Same as 9) above but for a random orientation of the incident light. Because of out-of-plane propagation, the value of $\phi_{in}$ and $\phi_p$ are not same.
11) sliced.m: This code produces a plot similar to Figure 3.4 of Chapter 3. Instead of just the quadrant, the full slice through the dispersion surface along with the edge of the Brillouin zone is constructed. Free-space dispersion curve is also plotted to demonstrate the calculation of the propagation angle. The user needs to input ‘w’, ‘b’ and the incident angle ‘ti’ in the code. A plot is generated as shown in Figure B.5. It is useful for visually checking the variation of propagation direction as a function of incident angle.

All the codes for \{001\} face are written to optimize the final result. Results for \{111\} face can be obtained by transformation of axes from \{001\} to \{111\}. The next section describes the codes written for generating results with respect to \{111\} face.

![Figure B.5](image)

Figure B.5 Plot generated by sliced.m. Slice is cut at $k_x = k_y$. The hexagon is the Brillouin zone edge and the circle is the free-space dispersion curve. The red curve is the slice through the photonic crystal dispersion surface. For any incident wave vector (blue line, in this case $\theta_{in}=25^\circ$), the propagation wave vector (cyan) is calculated using momentum conservation (green line) along the boundary of photonic crystal surface and air. The gradient at the end point of the propagation wave vector gives the propagation direction (black line).
B.2.2 Calculation with respect to \{111\} set of planes

There are various codes written to produce results with respect to \{111\} set of planes, both numerically as well as visually. The orthogonal triplet consists of \([-1,1,0]\), \([-1,-1,2]\) and \([1,1,1]\) directions as x, y and z directions respectively. As mentioned before, documentation within the codes is very extensive and the codes are self-explanatory. Hence minimum required explanation is presented here.

1) \texttt{ds111fnc.m}: same as \texttt{ds001fnc.m} but for \{111\} set of planes.

2) \texttt{ds111pnc1.m}: This code is used for generating partial dispersion surface and estimating its accuracy for the calculation of propagation angle \(\theta_p\) as a function of incident angle \(\theta_{in}\). Since [111] direction is not a symmetry axis for the dispersion surface, the result does not exhibit symmetry about \(\theta_{in}=0^\circ\). Hence, calculation of dispersion surface in one octant only is not enough. All the regions of dispersion surface above \(x=0\) needs to be constructed, and this code generates one of the four partial parts. The other relevant parts of the dispersion surface are generated using \texttt{ds111pnc2.m}, \texttt{ds111pnc3.m}, \texttt{ds111pnc4.m}, and \texttt{ds111pnc5.m}, and all these codes use non-continuous data.

3) \texttt{ds111pnc6.m}: Same as 2) above with the addition that propagation wave vectors and directions are plotted. It gives an idea about the beam orientation and confinement within the photonic crystal. Besides generating propagation orientation of the beam for input orientations, the code produces a plot to depict them visually. Since there can be
numerical errors due to low density of surface grids, the basic use of this code is to visually check for deviant behavior, if any, and estimate and improve its resolution and accuracy. The results may or may not be accurate.

4) ds111pc1.m: Same as 2) above but uses continuous data. Also, the surface grid data is generated for all the k-points and then they are transformed (to orthogonal triplet corresponding to \{111\} face) before plotting. This is in contrast with ds111pc3.m, which is the same as this code, but the data (k-points) is transformed first and then surface grid points are generated for plotting. Both approaches are compared to check which one produces more accurate results numerically.

5) ds111pc2.m: Same as 4) above with the addition that propagation wave vectors and directions are plotted. The results may or may not be accurate since this code is used for analyzing and optimizing results, both numerically and visually. ds111pc4.m uses ds111pc3.m for generating propagation wave vectors and directions.

6) ds111tpvti1.m: This code calculates the relation between $\theta_p$ and $\theta_{in}$ with respect to the normal of \{111\} face. The incident orientation is chosen in a way such that the beam is confined in one plane and its propagation can be parameterized by a single angle. Continuous data and denser grid size is used, and the incident and propagation angle values are saved in a data file for plotting outside matlab. Since more than one portion of the dispersion surface needs to be constructed for obtaining this result, other files viz. ds111tpvti2.m, ds111tpvti3.m, and ds111tpvti4.m are used for calculation of data for the
entire range of incident angles. The data generated by these codes is plotted in Figure 3.7 of Chapter 3. Figure 3.8 shows the same result for different values of ‘w’ in the codes.

7) ds111phd.m: This code generates a very small portion of the dispersion surface. This small portion of the dispersion surface (around a point governed by the incident angle) has a very high density of grid points (increment in k points is 0.0002) and hence highest possible accuracy (within numerical limits) in the calculation of internal propagation angles. Continuous data is used to preserve the smoothness in curvature which eliminates deviant behavior. This code is useful for calculating the variation in the propagation direction as a function of frequency, for a fixed incident orientation of the light beam. ds111phdl.m and ds111phd2.m generate similar results but for in-plane propagation and out-of-plane propagation of the light beam respectively. The basic use is to check the accuracy and to develop a similar code to calculate the whole range of propagation directions in a precise way.

8) ds111tpvw.m: Using 7) above as template, this code calculates the relation between θ_p and frequency for a fixed incident orientation. In ds111tpvw1.m (see the end of this Appendix), the incident orientation is such that the beam is confined in a plane, and hence the propagation direction can be parameterized by a single angle. Values are with respect to {111} face and the results are shown in Figure 3.5 of Chapter 3. Figure 3.9 shows similar results for different values of polymer refractive index. ds111tpvw2.m generates relation between the propagation direction and frequency for a random orientation. The beam is not confined in a plane and both θ_p and φ_p change, which is
depicted in Figure 3.11.

9) xvn111.m: This code plots the displacement in the beam centroid (as detected by the position sensitive detector) as a function of the polymer refractive index. The generated data is saved in a file to be plotted outside matlab. Figure 4.4 shows the data generated using this code.

10) expdata.m: This code simulates the experimental setup and computes the expected response, as shown in Figure 5.7 of Chapter 5. Both ‘h’ and the photonic crystal thickness used in the code are displayed in the command window, and the plot is generated too.

B.3 Summary

This concludes the explanation of all the codes pertaining to results presented in Chapters 3, 4, and 5. As mentioned before, all the matlab files are saved in SuperPrism\Dsplots\, and the codes specific to results presented in Chapters 3 and 4 are saved in the folder d001 under Dsplots. The codes are well documented and can be easily modified, if the need arises. This appendix will hopefully enable a better use of the programs for detailed understanding of the concept or improvement of the calculations.
Scheme code to calculate the complete photonic band structure for slightly sintered inverted-FCC lattice (KLW plane only)

(set! grid-size (vector3 16 16 16))
(set! mesh-size 7)
(set! num-bands 4)

(set! geometry-lattice (make lattice
  (basis1 0 1 1)
  (basis2 1 0 1)
  (basis3 1 1 0) ))

(define-param kxklw 0.5)
(define-param kyklw 0.5)

(define-param eps 2.4964) ; the dielectric constant of the polymer
(define-param r .53) ; the radius of the air spheres
(define die1 (make dielectric (epsilon eps)))

(let f1 ((kxklw 0.5)))
(define (kymin xvalue)
  (- 0.75 (* xvalue 0.5)))
(let f2 ((kyklw (kymin kxklw)))
(define (kzklw xx yy)
  (- 1.5 (+ xx yy)))

(set! k-points (interpolate 28 (list
  (vector3 0 0 0)) ; Gamma point
  (vector3 kxklw kyklw (kzklw kxklw kyklw)))) ; KLW plane

(set! geometry (list
  (make block (center 0 0 0) (size 1 1 1) (material die1))
  (make sphere (center 0 0 0) (radius r) (material air))))

(run)

(if (< kyklw 0.5)
  (f2 (+ kyklw .00625))
)

(if (< kxklw .75)
  (f1 (+ kxklw .0125)))
)
Scheme code to calculate the complete photonic band structure for slightly sintered inverted-FCC lattice (LUW plane only)

```
(set! grid-size (vector3 16 16 16))
(set! mesh-size 7)
(set! num-bands 4)

(set! geometry-lattice (make lattice
  (basis1 0 1 1)
  (basis2 1 0 1)
  (basis3 1 1 0) ))

(define-param kxluw 0.5)
(define-param kzluw 0.5)

(define-param eps 2.4964) ; the dielectric constant of the polymer
(define-param r .53) ; the radius of the air spheres
(define diel (make dielectric (epsilon eps)))

(let f1 ((kzluw 0.5))
  (define (kxmin zvalue1)
    (- 0.75 (* zvalue1 0.5)))
  (let f2 ((kxluw (kxmin kzluw)))
    (define ((kluw xx zz)
      (- 1.5 (+ xx zz)))

(set! k-points (interpolate 28 (list
  (vector3 0 0 0) ; Gamma point
  (vector3 kxluw (kluw kxluw kzluw) kzluw))))

(set! geometry (list
  (make block (center 0 0 0) (size 1 1 1) (material diel))
  (make sphere (center 0 0 0) (radius r) (material air))))

(run)

(define (kxmax zvalue2)
  (- 1 zvalue2 ))

(if (< kxluw (kxmax kzluw))
  (f2 (+ kxluw .00625)))

(if (> kzluw .25)
  (f1 (- kzluw .0125)))
```
Scheme code to calculate the complete photonic band structure for slightly sintered inverted-FCC lattice (WUX plane only)

(set! grid-size (vector3 16 16 16))
(set! mesh-size 7)
(set! num-bands 4)

(set! geometry-lattice (make lattice
  (basis1 0 1 1)
  (basis2 1 0 1)
  (basis3 1 1 0) ))

(define-param kwwux 0.5)
(define-param kzwux 0)

(define-param eps 2.4964) ; the dielectric constant of the polymer
(define-param r .53) ; the radius of the air spheres
(define diel (make dielectric (epsilon eps)))

(let f1 (list kwwux 0)
(define (kxmin zvalue1)
  (+ (* zvalue1 0.5) 0.5))
(let f2 ((xx (kxmin kwwux))
(define (kyyux xx zz)
  (+ 1 (- zz xx)))

(set! k-points (interpolate 28 (list
  (vector3 0 0 0) ; Gamma point
  (vector3 kwwux (kwwux kwwux kwwux) kwwux))))) ; WUX plane

(set! geometry (list
  (make block (center 0 0 0) (size 1 1 1) (material diel))
  (make sphere (center 0 0 0) (radius r) (material air)))

(run)

(define (kxmax zvalue2)
  (+ zvalue2 0.5))

(if (< kwwux (kxmax kwwux))
  (f2 (+ kwwux .00625)))

(if (< kwwux .25)
  (f1 (+ kwwux .0125)))

)
Matlab code ds001fnc.m

% code to generate the full dispersion surface, for a given w (freq) %

w=0.30; % this value should lie in the concerned band
b=6; % Band#4:b=9  Band#3:b=8  Band#2:b=7  Band#1:b=6
incr=0.0025; % spacing between k-points in the dispersion surface
ni=30; % number of data points from gamma to a point on the
% Brillouin zone (from MPB)

% For all directions in the klwn1590 plane
---------------------------------------------
load klwn1590.dat;
kx=klwn1590(:,2);
ky=klwn1590(:,3);
kp=klwn1590(:,4);
kmag=klwn1590(:,5);
wr=klwn1590(:,b);
fac=length(kx)/ni;
j=0;
for i=0:1:(ni-1)
    j=j+1;
    kxdata=kx((ni*i)+1:ni*(i+1));
    kydata=ky((ni*i)+1:ni*(i+1));
    kpdata=kz((ni*i)+1:ni*(i+1));
    kmagdata=kmag((ni*i)+1:ni*(i+1));
    wrdata=wr((ni*i)+1:ni*(i+1));
    kxr=interpl(wrdata,kxdata,w);
    kyr=interpl(wrdata,kydata,w);
    kxr=interpl(wrdata,kpdata,w);
    kxok(j)=kxr+kyr-kzr; % converting from rhombohedral coordinates
    kyok(j)=kxr-kyr+kzr; % MPB uses primitive FCC lattice to
    kzk(j)=kxr+kyr+kzr; % standard cartesian orthogonal triplet
    kxok(j)=sqrt((kxok(j)^2)+(kyok(j)^2)+(kzk(j)^2));
end

% For all directions in the luwn1590 plane
---------------------------------------------
load luwn1590.dat;
kx=luwn1590(:,2);
ky=luwn1590(:,3);
kz=luwn1590(:,4);
kmag=luwn1590(:,5);
wr=luwn1590(:,b);
fac=length(kx)/ni;
j=0;
for i=0:1:(fac-1)
    j=j+1;
    kxdatal=kx((ni*i)+1:ni*(i+1));
    kydata=kx((ni*i)+1:ni*(i+1));
    kzdata=kmag((ni*i)+1:ni*(i+1));
    kdata=kmag((ni*i)+1:ni*(i+1));
    wrdata=wr((ni*i)+1:ni*(i+1));
    kxr=interpl(wrdata,kxdata,w);
    kyr=interpl(wrdata,kydata,w);
    kzn=interpl(wrdata,kzdata,w);
    kxol(j)=kxr+kyr-kzn; %converting from rhombohedral coordinates
    kyol(j)=kxr+kyr+kzn; %MPB uses primitive FCC lattice to
    kzol(j)=kxr+kyr+kzn; %standard cartesian orthogonal triplet
    kmol(j)=sqrt((kxol(j)^2)+(kyol(j)^2)+(kzol(j)^2));
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% For all directions in the wuxn1590 plane
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

load wuxn1590.dat;
kx=wuxn1590(:,2);
ky=wuxn1590(:,3);
kp=wuxn1590(:,4);
kmag=wuxn1590(:,5);
wr=wuxn1590(:,6);
fac=length(kx)/ni;
j=0;
for i=0:1:(fac-1)
    j=j+1;
    kxdatal=kx((ni*i)+1:ni*(i+1));
    kydata=kx((ni*i)+1:ni*(i+1));
    kzdata=kmag((ni*i)+1:ni*(i+1));
    kdata=kmag((ni*i)+1:ni*(i+1));
    wrdata=wr((ni*i)+1:ni*(i+1));
    kxr=interpl(wrdata,kxdata,w);
    kyr=interpl(wrdata,kydata,w);
    kzn=interpl(wrdata,kzdata,w);
    kxow(j)=kxr+kyr-kzn; %converting from rhombohedral coordinates
    kyow(j)=kxr+kyr+kzn; %MPB uses primitive FCC lattice to
    kzow(j)=kxr+kyr+kzn; %standard cartesian orthogonal triplet
    kmow(j)=sqrt((kxow(j)^2)+(kyow(j)^2)+(kzow(j)^2));
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Plot the 3-D dispersion surface (Needs a lot of replication) %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

for ns=1:1:3
    if (ns==1)
        p(1,:)=kxow; $\text{wuxn1590 plane}$
        p(2,:)=kyow;
        p(3,:)=kzow;
    end;
    if (ns==2)
p(1,:) = kxol;  
 perché
p(2,:) = kyol;  
 perché
p(3,:) = kzol;  
 perché
end;
if (ns==3)
  p(1,:) = kxok;  
 perché
p(2,:) = kyok;  
 perché
p(3,:) = kzok;  
 perché
end;
for m=0:1:1
  for n=0:1:1
    for o=0:1:1
      for i=1:1:3
        if (i==1)
          j = 2;
          k = 3;
        end;
        if (i==2)
          j = 1;
          k = 3;
        end;
        if (i==3)
          j = 1;
          k = 2;
        end;
        for l=1:1:2
          if (l==2)
            temp = j;
            j = k;
            k = temp;
          end;
        end;
        [xi, yi] = meshgrid(min(p(i,:)*(-1)^m):incr:max(p(i,:)*(-1)^m),
                          min(p(j,:)*(-1)^n):incr:max(p(j,:)*(-1)^n));
        zi = griddata(p(i,:)*(-1)^m, p(j,:)*(-1)^n, p(k,:)*(-1)^o, xi, yi);
        surf1(xi, yi, zi)
        colormap(copper);
        shading interp;
        grid on;
        hold on;
      end;
    end;
  end;
end;
clear p;
end;

%title('band#4, w=0.80, n=1.590');
xlabel('kx');
ylabel('kx');
zlabel('kx');

% Generate the 1st BZ of FCC %
wx = [0.5 1 1 0.5 0 0 0.5];
wv = [0 0 0.5 1 1 0.5 0];
wz = [1 0.5 0 0 0.5 1 1];
for i=0:1
    for j=0:1
        for k=0:1
            plot3(wx*(1)^i,wy*(-1)^j,wz*(-1)^k,'ko-'
'', 'MarkerSize', 9, 'LineWidth', 2);
            view(-72,13);
            hold on;
            grid on;
            pbaspect([1,1.5,1.5]);
        end;
    end;
end;
Matlab code ds111tpw1.m

```matlab
% % code to plot theta_p vs w (for a particular incident angle and % % refractive index of the photonic crystal) and save the generated % % data in an appropriate file. Very small portion of the dispersion % % surface (around a point governed by the incident angle) having % % very high density of grid points is generated for highest possible % % accuracy of internal propagation angles % %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
count=0;
for w=0.79900:0.00005:0.80300
b=9;
  % Band#4:b=9 Band#3:b=8 Band#2:b=7 Band#1:b=6
incr=0.0002;
  % number of data points from gamma to a point on the
  % Brillouin zone (from MPB)

% For all directions in the klwn1580 plane
-----------------------------------------------
load klwn1580.dat;
kx=klwn1580(:,2);
ky=klwn1580(:,3);
kz=klwn1580(:,4);
kmag=klwn1580(:,5);
wr=klwn1580(:,6);
fac=length(kx)/ni;
j=0;
  for i=0:1:(fac-1)
    j=j+1;
    kxdata=kx((ni*i)+1:ni*(i+1));
    kydata=ky((ni*i)+1:ni*(i+1));
    kzdata=kz((ni*i)+1:ni*(i+1));
    kmagdata=kmag((ni*i)+1:ni*(i+1));
    wrdata=wr((ni*i)+1:ni*(i+1));
    kxr=interpl(wrdata,kxdata,w);
    kyr=interpl(wrdata,kydata,w);
    kzk=interpl(wrdata,kzdata,w);
    kxok(j)=kx+kz+kzr;  %converting from rhombohedral coordinates
    kyok(j)=kx+kzr;  %MPB uses primitive FCC lattice to
    kzok(j)=kzr;  %standard cartesian orthogonal triplet
    kmok(j)=sqrt((kxok(j)^2)+(kyok(j)^2)+(kzok(j)^2));
  end

% For all directions in the luwn1580 plane
--------------------------------------------
load luwn1580.dat;
kx=luwn1580(:,2);
```

This text contains Matlab code for plotting theta_p vs. w for a particular incident angle and refractive index of a photonic crystal. The code generates a small portion of the dispersion surface with very high density of grid points for the highest possible accuracy of internal propagation angles.
ky=luwn1580(:,3);
kz=luwn1580(:,4);
kmag=luwn1580(:,5);
wr=luwn1580(:,b);
fac=length(kx)/ni;
j=0;
for i=0:1:(fac-1)
j=j+1;
kxdata=kx((ni*i)+1:ni*(i+1));
kydata=ky((ni*i)+1:ni*(i+1));
kzdata=kz((ni*i)+1:ni*(i+1));
kmdata=kmag((ni*i)+1:ni*(i+1));
wrdata=wr((ni*i)+1:ni*(i+1));
kxr=interpl(wrdata,kxdata,w);
kyr=interpl(wrdata,kydata,w);
kzr=interpl(wrdata,kzdata,w);
xxol(j)=kxr+kyr+kzr; %converting from rhombohedral coordinates
kyol(j)=kxr-kyr+kzr; %MPB uses primitive FCC lattice to
kzol(j)=kxr+kyr-kzr; %standard cartesian orthogonal triplet
kmol(j)=sqrt((xxol(j)^2)+(kyol(j)^2)+(kzol(j)^2));
end

% For all directions in the wuxn1580 plane

load wuxn1580.dat;
kx=wuxn1580(:,2);
ky=wuxn1580(:,3);
kz=wuxn1580(:,4);
kmag=wuxn1580(:,5);
wr=wuxn1580(:,b);
fac=length(kx)/ni;
j=0;
for i=0:1:(fac-1)
j=j+1;
kxdata=kx((ni*i)+1:ni*(i+1));
kydata=ky((ni*i)+1:ni*(i+1));
kzdata=kz((ni*i)+1:ni*(i+1));
kmdata=kmag((ni*i)+1:ni*(i+1));
wrdata=wr((ni*i)+1:ni*(i+1));
kxr=interpl(wrdata,kxdata,w);
kyr=interpl(wrdata,kydata,w);
kzr=interpl(wrdata,kzdata,w);
xxow(j)=kxr+kyr-kzr; %converting from rhombohedral coordinates
kyow(j)=kxr-kyr+kzr; %MPB uses primitive FCC lattice to
kzow(j)=kxr+kyr-kzr; %standard cartesian orthogonal triplet
kmow(j)=sqrt((xxow(j)^2)+(kyow(j)^2)+(kzow(j)^2));
end

% Plot the 3-D dispersion surface (Needs a lot of replication) %
```c
p(1,:) = kxow;  
\text{\textcolor{red}{%%%}}  
p(2,:) = kyow;  
\text{\textcolor{red}{%%%}}  
p(3,:) = kxow;  
\text{\textcolor{red}{%%%}}  
end;
if (ns==2)  
p(1,:) = kxol;  
\text{\textcolor{red}{%%%}}  
p(2,:) = kyol;  
\text{\textcolor{red}{%%%}}  
p(3,:) = kzol;  
\text{\textcolor{red}{%%%}}  
end;
if (ns==3)  
p(1,:) = kxok;  
\text{\textcolor{red}{%%%}}  
p(2,:) = kyok;  
\text{\textcolor{red}{%%%}}  
p(3,:) = kzkol;  
\text{\textcolor{red}{%%%}}  
end;
for i=1:1:3  
  if (i==1)  
    j=2;  
    k=3;  
  end;  
  if (i==2)  
    j=1;  
    k=3;  
  end;  
  if (i==3)  
    j=1;  
    k=2;  
  end;
for l=1:1:2  
  if (l==2)  
    temp = j;  
    j = k;  
    k = temp;  
  end;
  for tdc=1:1:length(p(i,:))  
    itd = itd + 1;  
    txdata(itd) = p(i,tdc);  
    tydata(itd) = p(j,tdc);  
    tzdata(itd) = p(k,tdc);  
  end;
end;
clear p;
end;
clear kx ky kz kmag wr kxdata kydata kzdata kmdata wrd data kxr kyr kzn  
kxow kyow kzow kxok kyok kzkol kxol  
clear kyol kzol kmok kmol kmow

% Transforming BEFORE generating grid points
% converting from orthogonal triplet of
% [1,0,0], [0,1,0], [0,0,1] to the
% triplet [-1,1,0], [-1,-1,2], [1,1,1]
\begin{align*}
\text{txn} &= (-1*txdata + (1*tydata + (0*tzdata))/sqrt(2));  
\text{tyn} &= ((-1*txdata - (1*tydata + (2*tzdata))/sqrt(6));  
\text{tzn} &= ((1*txdata) + (1*tydata) + (1*tzdata))/sqrt(3);
\end{align*}
```
### Obtain kx and ky value for a particular theta_in and phi_in

```matlab
theta_in = 39; % degrees (wrt the +ve Z axis, towards +ve X-Y plane; +ve)
theta_in = 90 - theta_in; % degrees (wrt the +ve XY plane, matlab convention)
phi_in = 90; % degrees (wrt the +ve X axis, matlab convention)
```

```matlab
[k1, k2, k3] = sph2cart(phi_in * pi / 180, theta_in * pi / 180, w);
```

```matlab
[xn, yn] = meshgrid(k1 - 0.1:incr:k1 + 0.1, k2 - 0.1:incr:k2 + 0.1);
zn = griddata(txn, tyn, tzn, xn, yn);
clear txdata tydata tzdatatxn tyn tzn
```

#### Generating the surface normals, and hence the internal propagation angles.

```matlab
disp('----- generating surface normals -----');
[sx, sy] = size(xn);
[nx, ny, nz] = surfnorm(xn, yn, zn);
chel(1,:,:)=xn;
chel(2,:,:)=yn;
chel(3,:,:)=zn;
chel(4,:,:)=nx;
chel(5,:,:)=ny;
chel(6,:,:)=nz;
for chelycount=1:1:sx
    for chelzcount=1:1:sy
        exdata = chel(:, chelycount, chelzcount);
rdata = 0;
        for chelxcount=1:1:6
            if (isnan(exdata(chelxcount))==1)
                rdata = 1;
            end;
        end;
    end;
end;
```

```matlab
%%%% Given the specific condition here (for phi_in)
%%%% x ~ y => phi_in = 45 degrees or -135 degrees
%%%% x ~ 0 => phi_in = +/- 90 degrees
```

```matlab
if ((rdata==0) & (abs(chel(1, chelycount, chelzcount))<0.001))
    % x ~ 0
elseif ((rdata==0) & abs(chel(1, chelycount, chelzcount)-
    chel(2, chelycount, chelzcount)<0.005) % x ~ y
elseif ((rdata==0) & abs(chel(3, chelycount, chelzcount)+0.6)<0.01)
    % z ~ 0.6
elseif ((rdata==0) & abs(chel(2, chelycount, chelzcount)<0.005))
    % y ~ 0
```

```matlab
k1 = chel(1, chelycount, chelzcount);
k2 = chel(2, chelycount, chelzcount);
k3 = chel(3, chelycount, chelzcount);
[ph, th, rad] = cart2sph(k1, k2, sqrt((w*w)-(k1*k1)-(k2*k2)));
%%%% momentum conservation
phi_in = ph + 180/pi;
```
theta_i=theta_i*180/pi;
theta_in=90-theta_i;              % wrt the +ve Z-axis

n1=chel(4,chelycount,chelzcount);
n2=chel(5,chelycount,chelzcount);
n3=chel(6,chelycount,chelzcount);
[ph,th,rad]=cart2sph(n1,n2,n3);
phi_out=ph*180/pi;
theta_o=th*180/pi;
%theta_out=90-theta_o;           % suppressed for correct analysis

%% Further reduction of error
if (abs(theta_in-39)<0.001)
disp('------------')
w
phi_in
phi_out
theta_in
if (phi_out>0.0)    % +ve theta_out in 2-D slice
  theta_out=90-theta_o;   % wrt the +ve Z-axis
end;
if (phi_out<0.0)    % -ve theta_out in 2-D slice
  theta_out=theta_o-90;   % wrt the +ve Z-axis
end;
theta_out
disp('------------')

fcount=fcount+1;               % stuff to plot
wo(fcount)=w;                  % outside this
theta_out(fcount)=theta_out;  % code (check at
phi_ino(fcount)=phi_in;        % the end of this
phi_outo(fcount)=phi_out;      % program)
theta_ino(fcount)=theta_in;   % (file:139n1580.dat)

plot(w,theta_out,'g.');
grid on;
hold on;
break;
end;
end;
if (abs(theta_in-39)<0.001)
  break;
end;

end;
clear chel sx sy;
disp('------ finished generating surface normals ------');
end;

xlabel('w');
ylabel('internal propagation angle');
title('internal propagation angle Vs w');
% save the required stuff in a file to plot separately outside this code

fid=fopen('check111.dat','a');
fid=fopen('i39n1580.dat','a');
for i=1:length(wo)
    fprintf(fid,'%f\t',wo(i));
    fprintf(fid,'%f\t',phi_ino(i));
    fprintf(fid,'%f\t',phi_outo(i));
    fprintf(fid,'%f\t',theta_ino(i));
    fprintf(fid,'%f\n',theta_outo(i));
end;
fprintf(fid,'\n');
fclose(fid);