Opal photonic crystal fabrication and optical characterization

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by
Ragesh Kumar T P

Under the esteem guidance of

Dr. B. V. R. Tata
Scientific Officer (H)
Professor-HomiBhabhaNational Institute
Head, Light Scattering Studies Section
IGCAR, Kalpakkam, Tamilnadu-603102, India

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Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu
DECLARATION

I hereby declare that this submission ‘‘Opal photonic crystal fabrication and optical characterization’’ is a record of my project work carried out under the supervision of Dr.B.V.R.Tata, Scientific Officer(H), Head Light Scattering Section(LSSS), and it is my work and that, to the best of my knowledge and belief, and the same has not submitted elsewhere for any other degree.

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NIT Calicut

RAGESH KUMAR TP
(M090060PH)
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RAGESH KUMAR TP
(M090060PH)
Motivation

In future photonic crystal technology may replace semiconductor technology in the computer field and communication field. But lot of good and active research work is required to make use of photonic crystal in computer and communication field, any work to improving the quality of photonic crystal is very much important. The major problem associated with photonic crystal is, till now there is no photonic crystal having complete band gap in the visible region. Photonic crystal with complete band gap in the microwave region is reported. Theoretically it is predicted that Face Centered Cubic photonic crystal having refractive index contrast greater than 2.8 and Diamond structure photonic crystal with 2 will show complete photonic band gap in the visible region.

FCC opal photonic crystal can be fabricated easily by self assembling method. It is cheaper and efficient method. Vertical self assembly is the most advanced and efficient method in self assembly method. In our work also vertical self assembly method is used for making opal photonic crystal, a good deposition of PS spheres is observed. Best technique to optically characterize photonic crystal is recording reflection or transmission spectra. Band gap information can extracted from the spectra. Theoretically plotted the band diagram, using MPB software and compared with the reflection spectra.

Infiltration is the best method to increase the refractive index contrast, so that better band gap photonic crystal will get. The infiltrating material should have high refractive index and transparency.
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Chapter 1
1.1 Introduction

Photonic crystals (PCs) are periodic arrangement of dielectric or metal-dielectric synthetic structures with lattice constants in the visible range designed to influence the propagation of electromagnetic waves in the same way as the periodic electric potential in a semiconductor crystals influences the electron motion by defining allowed and forbidden energy bands. The simplest form of the photonic crystal is a one-dimensional periodic structure such as a multilayer film. The propagation of the electromagnetic waves in such structures was first studied by Rayleigh in 1887 [1]. It was shown that light propagation is angle dependent and prohibited for a range of frequencies. The possibility to create two- and three-dimensional photonic crystals with two- and three-dimensional forbidden band gaps needed one hundred years more to be proposed almost simultaneously by John [2] and Yablonovitch [3].

The possibility of photonic band gap was first proposed by Yablonovitch (at Bell Communications Research, USA) and John (at Princeton University, USA) in 1987, Yablonovitch published a paper in Physical Review Letters which dealt with the possibility of inhibiting spontaneous emission of EM radiation using a three-dimensionally periodic structure and John work discussed the strong ‘Anderson localization’ of photons in carefully prepared disordered dielectric super lattices [1]. These two works are considered as the origin of the research work in the field of photonic crystal and photonic materials. In 1990 Satpathy et al.[4 ] and Leung et al.[5] independently published an implementation of the plane wave method (PWM) with the scalar approximation to photonic band calculations. In 1994 several theoretical structures[6,7] with complete photonic band gap were proposed. The first realization of a crystal with a complete PBG in the microwave region was performed by Yablonovitch [3]. The samples were fabricated drilling three tilted holes 35.26 degrees off vertical in each position of an hexagonal lattice marked on the surface of a block of low loss dielectric material. The structure obtained was a face centered cubic (FCC) lattice with a basis of non spherical atoms and has taken the name of Yablonovite, in its inventor’s honor. A view of the drilling directions is illustrated in Fig. 1.1(a), together with the photonic band structure that presents a complete PBG, shown in Fig. 1.1(b)
1.2 Geometry of photonic crystals

Depending on whether the periodic variation of the dielectric constant is created in one, two or three dimensions, photonic crystals can be classified into three following categories. In each of the cases of the periodicity the spatial period of the elements is called the lattice constant, in analogy with the lattice constant of ordinary crystals composed of a regular array of atoms. In contrast with the case of ordinary crystals, the lattice constant in the photonic crystals case is on the order of the wavelength of the relevant electromagnetic waves for them.

1D Photonic crystal

The simplest possible structure of photonic crystal is one dimensional (1D), which is shown in the Fig. 1.2 consisting of alternate layers of different dielectric constants, a multilayer film. The one-dimensional photonic crystals are known for several decades [10]Heavens-1965; Perilloux-2002] in the form of periodic multilayer coatings, consisting of stacked pairs of alternate dielectric or metal-dielectric layers with a large contrast of the dielectric constant along the propagation direction. One-dimensional photonic crystals have a wide range of applications.
such as stop-band filters, high-reflection mirrors, antireflection coatings, and cavities for distributed feedback lasers [11].

![Fig. 1.2. 1D photonic crystal](image)

In the multilayer film (Fig. 1.2) the dielectric constant is varying in z direction, alternate layers are arranged in z direction.

### 2D photonic crystals

Two-dimensional (2D) photonic crystals consist of a regular array of dielectric or metal-dielectric materials in two directions while the structure is homogeneous and infinite in the other direction; a typical structure consisting of square lattice of dielectric rods is shown in Fig. 1.3. The height of the rods are assumed to be infinitely long thus it will have a photonic band gap in the XY plane [11].
Fig. 1.3. 2D photonic crystal

In the above figure the left side is a square lattice of dielectric columns, with radius $r$ and dielectric constant $\varepsilon$. The material is homogeneous along the z direction (the cylinders assumed to be of infinite length), and periodic along X and Y with lattice constant $a$. Much of the interest in 2D photonic crystals arises not from the presence of a bandgap alone, but rather from the ability to create localized defect states within the bandgap by introducing a structural defect into an otherwise regular lattice. For example, the removal of a single scatterer (point defects) from a 2D PC creates a point-like defect or a resonant cavity, and the removal of a line of scatterers (line defects) can create a waveguide that supports propagating modes.

3D Photonic crystal

Three-dimensional (3D) photonic crystals consist of a regular array of dielectric or metal-dielectric materials in the three directions. This structure is the only one that can exhibit a complete band gap, that is, a frequency range where the propagation of electromagnetic waves is forbidden, irrespective of the propagation direction. A large number of photonic crystals are possible in 3D but all the structures may not give the photonic band gap (PBG). Fig. 1.4 shows schematically the wood pile and opal FCC structures. These structures can have a photonic band gap, if there is sufficient refractive index contrast ($\Delta n > 2.8$). Theoretically it is predicted that diamond structure is the most suitable structure for giving complete band gap even for low refractive index contrast ($\Delta n > 2$). Thus researchers are trying to find out a simple method for making photonic crystals with diamond structure.

![Woodpile](image1)

![Opal](image2)

Fig. 1.4. Woodpile  Fig. 1.5. Opal
1.3. Opal and Inverse opal Photonic crystal

An opal structure is a crystal of dielectric spheres arranged in air(or solvent) with FCC ordering. In artificially synthesized opal structure, usually [111] planes are parallel to the substrate on which the opal structure is grown and hence the opal structure can be viewed as a stacking of layers in a close-packed arrangement (packing density of 74%): each layer perpendicular to the [111] direction is a triangular lattice. For an FCC structure the lattice constant is given by \( a = \sqrt{2} \times D \) where \( D \) is the diameter of the sphere arranged in FCC structure and hence the diameter of the sphere should lie between 300 to 1300nm for the crystals formed by these spheres to act as photonic crystals in the optical and IR region. Fig 1.6 (a) shows the top view of three consecutive [111] planes. Usually opal structure grows along the [111] crystallographic plane and thus this growth direction will be taken as vertical direction.

![Fig 1.6. Top view of [111] plane of FCC lattice](image)

The distance between two consecutive layers along [111] plane \( (d_{111}) \) is given by

\[
d_{111} = \frac{\sqrt{2}}{\sqrt{3}} \times D = \frac{a}{\sqrt{3}}
\]

Where \( D \) is the sphere diameter and \( a \) is the lattice constant of the crystal [9].

In usually grown opal photonic crystal the refractive index contrast is found to be very low and is predicted that FCC opal structures show a complete photonic band gap for a refractive index contrast of more than 2.8[12]. For increasing the refractive index contrast normally
infiltration of a high refractive index material into opal photonic structure is done. Hence opal structures are usually used as templates for preparing good band gap photonic crystals. The simplest and efficient method for preparing opal photonic structure is colloidal self assembling techniques as it is a natural tendency of monodisperse colloidal particles to self organizes into ordered arrays. Polystyrene, Silica, Poly(methyl methacrylate) (PMMA) spheres are normally used for fabrication of opal structures via self assembly methods[13,14].

**Inverse opal Photonic structure**

Theoretically it is predicted that if the refractive index contrast between the sphere and void of FCC crystal is greater than 2.8 complete photonic band gap will appear whereas for diamond structures a refractive index contrast of 2 is enough to get full photonic band gap. Hence for observing a complete photonic gap it is requires make an inverse opal structure where air spheres (refractive index, n1=1) are embedded in an interconnected higher dielectric background (refractive index, n2).

1.4 Natural photonic crystal

In nature we can find many examples for natural photonic crystals. Opal is an example of natural PC with monodispersed amorphous Si spheres arranged in FCC strcture. The colors exhibited by opals are due to Bragg diffraction of visible light under white light illumination. Photonic structures are also present in peacock feathers, sea shells, stripes on some fish species, morpho butterflies, jewel beetles, etc.

1.5. Pseudo gap and complete band gap

When light enters into a photonic crystal it is scattered at the interfaces between different dielectric regions. Due to the periodicity, scattering can be coherent for certain directions and frequencies. As a result, some propagation directions are forbidden for photons of certain energies. In the photonic band structure diagram this is represented as a range of energies not covered by any band in that direction: this is called a photonic band gap. In some photonic crystal the wave with certain frequencies are forbidden in some particular directions, the gap
corresponding to that frequency is called pseudo gap. Fig 1.9 shows schematically the pseudo gap and the complete photonic band gap.

Fig. 1.9. Pseudo gap and complete band gap (Taken from Ref. [15])

Not all the photonic crystals show complete photonic band gap. It mainly depends upon the crystal symmetry and the refractive index contrast between the spheres and voids. Fig 1.9 (b) shows a complete photonic band gap, plotted for FCC crystal with higher refractive index contrast.

1.6. Applications of Photonic Crystals

Photonic band gap crystal allow control over the propagation of light. Photons have no rest mass and travel with speed of light. There are no photon-photon interactions at intensities of practical interest. PBG crystals allow to develop optical devices such as as diodes, transistors and switches and they would work much faster than silicon based electronic devices. This will pave the way for photonics and integrated optics era.

A range of applications have been demonstrated using photonic crystals as microcavities to produce Light Emitting Diodes (LED) and Laser Diodes (LD) which have significantly enhanced performance. Photonic crystal diodes and transistors will eventually enable the
construction of an optical computer in near future. Optical computers will be faster and can support neural networks resembling human brain, unlike electronic counterparts, which are restricted in architecture due to electrical cross-talk between nearby wires (John S et al., 2002). Single Mode Light Emitting Diode (SMLED), fabricated using photonic crystals will be more reliable, and have high efficiency.
2.1. Theoretical Calculation of Photonic Band gap

Photonic crystals are designed in order to gain control over the properties of photons in much the same way as ordinary semiconductors affect the properties of electrons. In this way, photonic crystals have forbidden band gaps that can be compared with the energy gaps between consecutive energy bands of the semiconductors. For photonic crystal to have the band gap in the optical region of electromagnetic spectrum the modulation of dielectric function should be of the order of a micron. Photonic crystal will work in the microwave region if there is a modulation of refractive index with period of the order of some centimeters. A simple model for explaining the band structure is 1D periodic variation of dielectric function. If the variation of refractive index is periodic the light reflected from set of parallel planes can constructively interfere, this phenomenon is called Bragg diffraction. The wavelength which will be reflected depends upon the periodicity of the refractive index variation. If the periodicity is in the optical region photonic crystal will show a band gap in the optical region.

The optical properties of photonic crystals are described by the dispersion relation, which is the relation between the frequency and the wave vector: \((\omega-k)\) relation.

For photons propagating in vacuum the dispersion relation is

\[ \omega = ck , \]

where \(\omega\) is the frequency of the wave, \(k\) is the wave vector, and \(c\) is the velocity of light in vacuum.

The dispersion relation for a wave propagating in homogeneous and isotropic dielectric medium with refractive index \(n\) is:

\[ \omega = \frac{ck}{n} \]

The dispersion relation is shown as dotted line in Fig. 2.1. For photonic crystals where the refractive index varies periodically, the dispersion relation gets modified accordingly which
is shown in the same figure represented by solid line. Physically we can say that this deviation is due to Bragg diffraction. In ordinary crystals the Bragg diffraction takes place due to the periodic variation of the electric potential whereas in case of photonic crystals the Bragg diffraction is due to the periodic variation of refractive index.

![Bragg Diffraction Diagram](image)

Fig 2.1. Dispersion relation in free space and periodic refractive index medium (Taken from Ref. [16])

**Bragg diffraction**

As in ordinary crystal, the band gap in Photonic crystal is also due to Bragg diffraction. Bragg diffraction is the fundamental mechanism determining the optical properties of photonic crystal, which is due to the interference between the waves reflected from set of parallel planes. Bragg reflection of electromagnetic radiation was first studied for atomic crystal which is showing Bragg reflection in X-ray region. Then started to study its for optical waves in a layered media of dielectric layers. A set of layers acts like a mirror if the Bragg condition is satisfied.
\[ m\lambda = 2d \sin \theta \] ………… 2.1

Where \( m \) is an integer, \( d \) is the distance between the lattice planes and \( \theta \) is the angle between normal to the plane and incident light. Reflection of optical waves occurs because of constructive interference, whenever the angle \( \theta \) is such that the path length difference \( 2d \sin \theta \) between the reflected optical wave equals an integer number of wavelength \( \lambda \). Selective reflection of wave causes distinct appearance of photonic crystal which is called iridescent or opalescent. Depending on illumination and the angle of incident light photonic crystals show different colors.

In the case of photonic crystal if the periodicity of refractive index is perfect, the efficiency of Bragg diffraction is 100%, i.e. when diffraction from many lattice planes interferes constructively. If a wave in a particular direction diffracted and constructively interfere, that wave in that direction will be forbidden. Therefore Bragg diffraction is the reason for appearance of stop gap in photonic crystals (a forbidden frequency window in the dispersion relation). When the wave vector \( k = \frac{2\pi}{\lambda} \) reaches \( \frac{\pi}{d} \) the Bragg condition will be satisfied. At this wave vector the dispersion relation shows a split with two branches separated by a stop gap. This is shown in Fig. 2.1.

Consider a light wave propagating through one dimensional photonic crystal (Fig. 2.3) consisting of alternatively layers of dielectric materials of refractive indices \( n_1 \) and \( n_2 \). If wavelength of the light matches with the periodicity of refractive index of the layers, then Braggs condition is satisfied and the wave will reflect back. This results in formation of a standing wave. Standing wave(1) has its antinodes in \( n_1 \) and nodes in \( n_2 \). Another wave with phase difference \( \frac{\pi}{2} \) also form standing wave(2) with antinodes in \( n_2 \) and nodes in \( n_1 \), which is predominantly is in the material \( n_2 \). Both standing wave have identical wavelengths but mainly exist in a different medium, \( n_1 \) or \( n_2 \). Since the frequency of light \( \omega \) is equal to

\[ \omega = \frac{cK}{n} = \frac{c}{n} \times \frac{2\pi}{\lambda} \] ………………………………2.2
where c is the velocity of light in vacuum, n is the refractive index of medium, λ is the wavelength. From above equation it is clear that for a crystal with periodically varying refractive indices, there are two frequencies at a given wavelength at the Bragg condition. Due to this two different frequencies a stop gap is formed at the Bragg condition which is shown in the figure 2.1, where the higher frequency corresponds to the wave in \( n_{\text{low}} \) and lower frequency to the wave in \( n_{\text{high}} \) medium.

![Standing wave formation at Bragg condition](image)

**Fig 2.3.** Standing wave formation at Bragg condition

The width of the stop gap denoted as \( \Delta \omega \) is a very important measure for photonic crystal indicated in figure 2.1, which is the difference of the frequency between the two standing wave formed in the photonic crystal [16, 17, 18, and 19].

### 2.1.2. Mathematical formulation of photonic band gap

Mathematically the band gap can be explained with Maxwell’s equations. In mixed dielectric media assume that there is no free charge and free current thus we can set \( \rho = 0 \) and \( J = 0 \). Next we have to relate \( \mathbf{D} \) to \( \mathbf{E} \) and \( \mathbf{B} \) to \( \mathbf{H} \) with a constituent relation, where \( \mathbf{E} \) and \( \mathbf{H} \) is electric and magnetic field, \( \mathbf{D} \) and \( \mathbf{B} \) are electric and magnetic displacement respectively. \( \mathbf{D} \) and \( \mathbf{E} \) are related by

\[
\mathbf{D} = \varepsilon \mathbf{E}
\]  

..................................................  2.3
\[ B = \mu H \] ........................................... 2.4

Where \( \varepsilon \) and \( \mu \) are electric permittivity and and magnetic permeability of the medium. Refractive index is related with \( \varepsilon \) and \( \mu \) as

\[ n = \sqrt{\varepsilon \mu} \] ........................................... 2.5

With the above assumption together with equation 3.3 and 3.4 we can write the Maxwell’s equation in the form as

\[ \nabla \cdot \mathbf{H}(r,t) = 0 \] ........................................... 2.6

\[ \nabla \cdot \varepsilon(r)\mathbf{E}(r,t) = 0 \] ........................................... 2.7

\[ \nabla \times \mathbf{E}(r,t) = -\mu \frac{\partial \mathbf{H}(r,t)}{\partial t} \] ........................................... 2.8

\[ \nabla \times \mathbf{H}(r,t) = \varepsilon \frac{\partial \mathbf{E}(r,t)}{\partial t} \] ........................................... 2.9

Equations 2.6 to 2.9 are called Maxwell’s equation.

For mathematical convenience it is better to take the field as a complex valued function, its real part will give the real physical field. Taking the solution in the form of time harmonic fields, we can write the field as

\[ \mathbf{H}(r,t) = \mathbf{H}(r)e^{-i\omega t} \] ........................................... 2.10

\[ \mathbf{E}(r,t) = \mathbf{E}(r)e^{-i\omega t} \] ........................................... 2.11

For finding the behavior of fields inside the medium substituting 2.10 and 2.11 into the curl equations of Maxwell’s equations we get

\[ \nabla \times \mathbf{E}(r,t) = i\omega \mu \mathbf{H}(r,t) \] ........................................... 2.12

\[ \nabla \times \mathbf{H}(r,t) = i\omega \varepsilon \mathbf{E}(r,t) \] ........................................... 2.13

From equation 2.13

\[ \mathbf{E}(r,t) = \frac{\nabla \times \mathbf{H}(r,t)}{i\omega \mu} \] ........................................... 2.14
From equation 2.12

\[ H(r, t) = \frac{\nabla \times E(r, t)}{i \omega \varepsilon} \] \hspace{1cm} \text{2.15}

Substituting equation 2.14 and 2.15 into the curl equation of Maxwell’s equation, we get

\[ \nabla \times \left( \frac{\nabla \times H(r, t)}{i \omega \varepsilon} \right) = -i \omega \mu H(r, t) \] \hspace{1cm} \text{2.16}

\[ \nabla \times \left( \frac{\nabla \times H(r, t)}{\varepsilon(r)} \right) = \left( \frac{\omega}{c} \right)^2 H(r, t) \] \hspace{1cm} \text{2.16}

\[ \nabla \times \left( \frac{\nabla \times E(r, t)}{i \omega \mu} \right) = -i \omega \varepsilon E(r, t) \] \hspace{1cm} \text{2.16}

\[ \nabla \times \left( \frac{\nabla \times E(r, t)}{\varepsilon(r)} \right) = \left( \frac{\omega}{c} \right)^2 E(r, t) \] \hspace{1cm} \text{2.16}

\begin{align*}
\nabla \times \left( \frac{\nabla \times H(r, t)}{\varepsilon(r)} \right) &= \left( \frac{\omega}{c} \right)^2 H(r, t) \\
\nabla \times \left( \frac{\nabla \times E(r, t)}{\varepsilon(r)} \right) &= \left( \frac{\omega}{c} \right)^2 E(r, t)
\end{align*}

The above equations shown in the box are called as master equation because it tells us everything we need to know about \( H(r, t) \) and \( E(r, t) \). From this equation we can get what are the modes permitted inside the medium and the forbidden frequency inside the dielectric medium concerned, called stop gap.

In both the master equation the variable that defines the structure of the crystal is dielectric constant \( \varepsilon(r) \). In photonic crystal it will be periodic, thus its inverse can be expanded in Fourier series as

\[ \frac{1}{\varepsilon(r)} = \sum_G k(G) e^{iG \cdot r} \] \hspace{1cm} \text{2.18}

Where \( G \) is reciprocal lattice vector, \( k(G) \) is the Fourier expansion coefficient.
According to Bloch theorem we can write $E(r)$ and $H(r)$ as

$$E(r) = u_{kn}(r)e^{ikr} \quad \text{............................................2.19}$$

$$H(r) = v_{kn}(r)e^{ikr} \quad \text{............................................2.20}$$

Where $u_{kn}$ and $v_{kn}$ are periodic function this also can be expanded in Fourier series as

$$u_{kn} = \sum_G E_{kn}(G)e^{iG \cdot r}$$

$$v_{kn} = \sum_G H_{kn}(G)e^{iG \cdot r}$$

By substituting the two above equation into 2.19 and 2.20, $E(r)$ and $H(r)$ become

$$E_{kn}(r) = \sum_G E_{kn}(G)e^{i(k+G) \cdot r} \quad \text{............................................2.21}$$

$$H_{kn}(r) = \sum_G H_{kn}(G)e^{i(k+G) \cdot r} \quad \text{............................................2.22}$$

Substitute these two equations into the master equation eigenvalue equations for the expansion coefficient of $E_{kn}(G)$, and $H_{kn}(G)$ will get [20]

$$-\sum_G k(G - G').(K + G') \times [(K + G') \times E_{kn}(G')] = \left(\frac{\omega_{kn}}{c}\right)^2 E_{kn}(G) \quad \text{...........2.23}$$

$$-\sum_G k(G - G').(K + G) \times [(K + G') \times H_{kn}(G')] = \left(\frac{\omega_{kn}}{c}\right)^2 H_{kn}(G) \quad \text{...........2.24}$$

Equations 2.23 and 2.24 are the set of eigenvalue equations. The solution to these eigenvalue equations (solved numerically and free soft ware packages are available) gives the eigenvalues and eigenvectors. The eigenvalues give the dispersion diagram and the eigenvectors can be substituted back into the Fourier expansion for electric field to find the field distribution at any given frequency. The only remaining problem is to find the dielectric coefficients, which can be obtained using the inverse Fourier transform of dielectric function.
Chapter 3

Experimental techniques for fabricating Photonic crystal

3.1. Opal photonic crystal fabrication

Fabrication methods of photonic crystals can be widely classified into two categories. One of which is top down approach involving techniques like holographic and lithographic techniques and the bottom-up approach which involves fabrication of opal structures by colloidal self assembly. A detailed description of the two approaches are given below.

1) Top-down approach

Yablonovite the first complete photonic band gap crystal in the microwave region was fabricated with top- down approach. Top-down approach starts with the bulk material, involves few steps of removal of the excess portion of the material using physical, chemical or mechanical methods to get desired opal structures. This route offers high control over the composition and geometry of the fabricated nanostructure; but it uses very expensive equipments, material and it’s a time consuming technique [22]. Lithographic techniques and holographic techniques are example of this approach.

i. Lithographic techniques

Lithographic technique involves layer by layer fabrication of the crystal, where the relative alignment between the layers plays a crucial one. In this method a thin film (say silica) is first deposited onto a silicon wafer. A pattern of parallel stripes is lithographically created on the silicon wafer and etched away, to create a series of parallel silica ridges. The space between them is filled with silicon and it is planarized by chemical or mechanical methods. The bar is then rotated at an angle of $90^\circ$ and a second layer of silica is deposited then the same process described above is repeated. After repeating several times a silicon/silica composite is obtained[23]. The resultant composite is immersed in hydrogen fluoride, by which all the silica
gets dissolved in hydrogen fluoride solution. Finally a Silicon photonic crystal is resulted. Fig 3.1 below shows the lithographically constructed Silicon photonic crystal.

![Lithographically constructed Silicon photonic crystal](image)

**Fig 3.1. Lithographically constructed Silicon photonic crystal (Taken from Ref. [23])**

**ii. Holographic techniques**

In Holographic technique several beams are allowed to interfere on a photo resist material. The photo resist is polymerized to fix the pattern, creating a replica of the intensity pattern above certain threshold, as shown in Fig.3.2. When two beams are allowed to interfere as shown in figure 2.2 lines of parallel interference pattern is formed and after polymerization this results in a one dimensional photonic crystal. When three beams are used the net result is parallel slabs of polymerized and non-polymerized monomer alternated in the direction of the wave vector difference giving rise to a 2D pattern. If four non collinear beams are used three dimensional interference pattern will be formed and hence a three dimensional pattern is created. The period of the structure and its symmetry (lattice) are decided by the laser wavelength, the relative phases, and incidence directions of the interfering beams

The advantages of this method are numerous. Firstly a 3D photonic crystal can be obtained in a very short period of time (a few minutes). Secondly, the number of parameters allows considerable freedom to design different symmetries and unit cell distribution. Thirdly, the process is relatively cheap. And finally, the method is scalable for large-scale production [23].
This method is still being developed but till now there is no report of a complete band gap photonic crystal with this method.

![Holographic process for making photonic crystal](image)

**Fig 3.2. Holographic process for making photonic crystal (Taken from Ref. [23])**

Bothe the techniques described above having some disadvantages like it is costly and not accurate.

2) **Bottom-up approach**

Bottom-up approach starts with the small building blocks which are nanometer scale objects, such as atoms, molecules, polymers, and colloids and achieves the bigger nanostructures by assembling them. Colloidal self assembly techniques are example for this approach

i. **Colloidal self assembly techniques**

There is a natural tendency for microscopic colloidal particles of silica, polystyrene (PS) or polymethylmetacrylate (PMMA) to self-assemble in an ordered face-centered cubic (fcc) structure. This tendency is utilized in self assembly techniques. Peoples like Pusey, Okubo and Nagayama give a great contribution to this field. The first requirements to make good self
assembled photonic structure is monodispersity in size of the building blocks. Widely used polymers for making photonic crystals are Polystyrene (PS), Silica and Polymethylmetacrylate (PMMA). Woodcock theoretically demonstrated that when hard spheres self-assemble in thermodynamically equilibrium the most stable structure it will assemble is Face Centered Cubic structure. The method for making photonic crystal from colloidal crystal is cheaper and accurate. There are mainly five simple methods for fabricating colloidal crystal

a) Sedimentation of colloidal particle under the influence of gravity

This method represents a classical approach of sedimentation of colloidal particles under the influence of gravity assembling into highly ordered structures mostly in FCC structures, a thermodynamically most stable structure. In this method the colloidal spheres are allowed to settle down on the bottom of the container; eventually the solvent (usually water) is dried at room temperature with very slow evaporation rate. Large sized particles settle down quickly whereas the smaller particles take long time. When the rate of sedimentation is slow the particles at the bottom of the container can undergo disorder to order transition driven by the minimization of the thermodynamic energy. But if the particles are sufficiently small or the density of the particles is comparable to that of the dispersion medium, the sedimentation will not occur and the particles exist as stable dispersion. Normally silica particle with size larger than 500nm can be crystallized with this sedimentation method. This method have some drawbacks, it gives little control on the quality of the top layer. Also it requires more time to make sufficiently large colloidal crystals (several weeks to months). The Sedimentation rate is given by the equation [24].

\[
v = \frac{2}{9} \times \frac{g a^2 (\rho_p - \rho_L)}{\eta}
\]

where ‘a’ is the diameter of the particle, g is acceleration due to gravity, \( \eta \) is the viscosity of the medium \( \rho_p \), and \( \rho_L \) is the particle and medium density. From the above equation it is clear that sedimentation rate depends upon diameter of the particle, density of the particle and medium, viscosity of the medium. Figure 3.3 shows the sedimentation of colloidal particle under the influence of gravity. [24]. Quality of the opal structure depends on the sedimentation rate. Gravity-sedimented samples generally contain polycrystalline domains of unknown sizes. Growth is difficult to adjust, and thus thickness is not easily controlled. The major disadvantage
of this method is formation of large number of unwanted and uncontrolled defects in the resulting crystals.

![Diagram of sedimentation process](image)

Fig 3.3. Sedimentation of colloidal particle under gravitational force

b) **Sedimentation of colloidal particle with the application of electric field**

Application of an external force through electric field or centrifugation parallel to the sedimentation vector can increase the sedimentation rate of the colloidal particles. This reduces the time of formation of colloidal crystal. One of the advantage of this method is that sedimentation under electrical fields can be used for the fabrication of colloidal crystals on patterned substrates with lattices other than FCC. Figure 3.4 shows the sedimentation of colloidal particle with the application of electric field[21].
c) **Vertical self assembly method**

Based on work and theory of Nagayama, Covin and co-workers used this method of vertical deposition method for growing the colloidal crystal. The formation of colloidal monolayer’s vertical deposition is based on the convective self assembly of colloids on a substrate by the action of moving meniscus. In a typical procedure a flat substrate either a glass or quartz is introduced in a vial containing a colloidal suspension which wets the substrate, a meniscus is formed at the line where the substrate, air and liquid meet. Crystal growth begins at the point of the meniscus where its thickness is below the diameter of the sphere. Menisci are also formed between the spheres which are pulled towards the substrate because of the capillary forces which tend them to get ordered in a closed packed structure. Due to evaporation of the solvent, the solvent molecules start flowing towards the meniscus region dragging the spheres from the suspension, which are incorporated into the ordered monolayer. If the colloidal concentration and evaporation rate is appropriate, more than one layer will begin to form at the point of meniscus. The Fig 3.5 below shows an experimental setup for vertical colloidal deposition. It consists of a 1 or 2cm diameter vial and a glass or quartz substrate inserted in the vial. Fig 3.6 shows the mechanism of colloidal particle deposition on the substrate.

![Fig 3.4. Sedimentation of colloidal particle under applied electric field](image-url)
Fig 3.5. Vertical colloidal deposition set up

Fig 3.6. Mechanism of colloidal particle deposition in vertical self assembly

**Factors influencing the growth of colloidal crystal in vertical deposition are**

a. *Concentration of the colloids*: In general higher concentration and smaller colloids yield samples with large number of layers, the optimum concentration for getting a good colloidal crystal is 0.20 to 0.27 wt%
b. *Diameter of the colloidal particle:* Larger sized colloidal particle have higher sedimentation rate, and hence in this method mostly colloidal particles with size smaller than 500nm are preferred to prevent sedimentation due to gravity. Although there are methods to overcome the sedimentation problem for higher diameter colloidal particles, this method is good for particles with smaller size.

c. *Temperature:* The Optimum temperature used for wide range of colloidal crystal self assembly is 45°C to 90°C. Samples grown at lower temperatures show a smaller number of layers as well as poorer quality as compared to that grown at higher temperatures where thicker samples are obtained at the price of lowered optical quality for the same concentration of the colloidal suspensions. This is probably due to the fact that for lower temperatures, sedimentation competes with convective fluxes and the reservoir of particles in the meniscus decreases with time.

d. *Substrates angle of inclination:* Substrates inclined 20° to 30° with respect to vertical produce better deposition of the colloidal particles on the substrate.

e. *Meniscus curvature:* This is a key parameter to be maintained during the drying of the sample. For getting a good quality deposition, the meniscus angle should be kept as low as possible [25], which is achieved by using a large diameter container used for keeping the colloidal suspension.

**The advantages of vertical deposition methods are**

i. We can control the sample thickness, thus one or more than one layer we can grow on the substrate by controlling the temperature and the colloidal concentration.

ii. Samples with sizes of several square centimeters can be fabricated in one or two days. Large area photonic crystal can be fabricated with substrates of larger area and vials with large diameter.

iii. Substrates on which these crystals are grown are rigid (usually a glass or silicon slide) and hence their manipulation becomes easier.

iv. With the same amount of material used to obtain an opal by natural sedimentation several thin film opals can be fabricated.

v. Since opals are much thinner, the number of defects observed in optical measurements is much lower.
vi. Infiltration of air voids with guest materials (materials with higher refractive index) is easier in thin film opals as these material need to penetrate just a few layers. [24,25]

d) Free standing colloidal crystal

In this method colloidal particles like Polystyrene (PS), Polymethylmetacrylate (PMMA) assembles at the air water interface. For a good assembly a specific density matching between colloidal particles and suspending medium is required. The thickness of the colloidal crystal formed depends upon the heating time which can be controlled easily and the crystal formed by this method remains stable without precipitation and agglutination even at room temperature for several months. The growth of colloidal crystal on the air water interface can be understood from the fact that on heating the liquid, the entropy of the microspheres increases resulting in an increased kinetic energy of colloidal particles. The colloidal particles may collide with each other to form di-microspheres then tri-microspheres and so on finally the aggregation leading to the formation of a colloidal crystal. The surface tension of the liquid keeps them on the air liquid interface, leading to the formation of aggregation of colloidal particles facilitating the formation of a homogeneously closely packed colloidal crystal with large surface which can be determined by the surface of the air liquid interface. A uniform heating results in the formation of layer by layer growth leading to the formation of three dimensional colloidal crystals. The growth rate of colloidal crystal can be enhanced by increasing the heating temperature. Inverse opal photonic crystal can also be made by adding precursor before heating. Hence this technique is a simple and efficient one for making of opal and inverse opal photonic crystals. Fig 3.7 shows the formation of free standing colloidal crystal.
e) **Vertical deposition by Dip drawing**

In this method clean substrate is placed perpendicular in the container having colloidal suspension. The substrate is drawn from suspension in a controlled fashion with slow drawing rate. Then the substrate is dried for some time in room temperature. Repeating the above procedure for several times will form successive layers of film, which makes the control over the thickness. Drawing the substrate and crystallization should keep a balance during this process (Zhifeng Liu *et al*, 2006). This method is comparatively fast and simple to implement even for large substrate areas. Figure 2.8 shows vertical deposition of colloidal particle by dip drawing.
f) Inward Growing Self-Assembling Method

This method is also called as horizontal deposition method. A little amount of colloidal suspension is placed and carefully spread over the substrate and allowed to dry at room temperature. Drying takes place at the periphery first and moves towards the central region of the film, which results in the void formation as shown in the figure 3.9. Multiple depositions are also possible. Large-scale (several centimeters in area) colloidal crystal films of controllable thickness have been fabricated within 2 hours without the use of any special facilities.

Criteria for becoming the colloidal crystal as a photonic crystal

1. Monodispersity is one of the important factor for the formation of ordered close packed crystal; monodispersity should not be vary more than 5-8%. Because of these reasons, Silica and polymer spheres are commonly used as a template for making photonic crystal
2. Refractive index contrast between low and high refractive index region should be sufficiently high (refractive index contrast should be greater than 2.8)
3. Volume fraction i.e. ratio of volume occupied by the spheres to the total volume must be between 63 to 74%.

Advantages and limitations of colloidal methods

Photonic crystals grown by colloidal methods are of special interest because of its ease, cost effectiveness and attractions compared to the lithographic techniques. Further, no repetitive steps are involved as in lithographic techniques. Visible and near infra-red photonic crystals impose fabrication challenges that are difficult to overcome by traditional lithographic techniques, particularly in three dimensions, although limited number of layers have recently been fabricated. The limitation of colloidal method is the difficulty in availability of monosized (monodisperse) particles of different chemical compositions and the defect formation. Intentional defect implementation and defect control is not trivial.
4.1. Optical techniques used for characterizing photonic crystal

1. Atomic Force Microscope (AFM)

AFM is widely used as an imaging techniques, it is designed to produce high resolution images of both conducting and non-conducting surfaces. The main advantage of this technique over optical microscopy is its higher resolution. Compared to other imaging techniques like SEM, or STM, AFM does not require any special sample preparation nor it requires the sample to be conductive one. It can work in ambient conditions and no vacuum is needed. It is operated with a fine tip mounted on a cantilever, which is brought very close to the sample surface. When the tip comes in contact with the surface some forces between the cantilever and sample surface comes into play, causing the deflection of the cantilever tip. When the tip is moved across the sample the rate of deflection in response to the height of the surface increases or decreases. This deflection can be easily detected by a simple set up consisting of a laser and a photo detector. The laser is reflected from the cantilever and allowed to fall on a quadrant photo detector, where the position of the spot of the laser beam on the photo diode changes in accordance with the cantilever deflection. There exists a feedback mechanism, which adjusts the z position of the cantilever tip, with a peizotube (PZT) scanner to maintain a constant cantilever deflection in response to the displacement of the laser spot over the photo diode. The amount of z-axis movement required to maintain a constant deflection at each point is stored and collectively forms an image of the sample surface. Figure 4.2 below shows the schematics of a Atomic Force Microscope.
2. **UV-Visible Spectroscopy**

UV-Visible Spectroscopic studies are essential to understand the optical properties of the sample such as reflection, transmission and absorption in the electromagnetic region of 190-800 nm. UV-Visible spectrophotometer analysis is one of the best technique to evaluate the quality of the photonic crystal. Reflectivity and transmission studies can directly show the existence of stop bands. A reflection peak or transmission minima corresponds to the band gap of the crystal. By taking reflection spectra at different incident angle, existence of any complete band gap or pseudo gap can be realised. For a particular wavelength if there is a reflection peak in all incidence angles, then material is said to have a complete band gap for that wavelength. Theoretically which wavelength will be reflected from the crystal at a given angle can be calculated using the equation

\[
\lambda = 2d_{111} \times \sqrt{n_{eff}^2 - \sin^2 \theta}
\]

Where \(d_{111}\) is the spacing between the [111] planes, \(n_{eff}\) is the effective refractive index, and \(\theta\) is the angle between the incident light and the normal to the substrate.
A photonic band gap in a given direction of propagation is called as stop band. Since stop bands are the precursors to a photonic band gap, the study of their optical properties is essential. The presence of stop-band in certain position of transmission spectra of samples also specifies the quality of packing (Shelekhina V M et al, 2001).

Figure 4.3. Optical system of UV-Visible spectrophotometer.


Single lamp cant provide the radiation covering UV Visible range so generally two light source will use in UV-Visible spectrometer one for UV radiation (a hydrogen or deuterium discharge lamp) and other for Visible light (tungsten or halogen lamp). Here in our case we have used a Jasco V-650 Spectrophotometer with light Source Deuterium lamp for 190 nm to 350 nm and Halogen lamp for 330 to 900 nm has been used. The Optical system of the UV-Visible Spectrophotometer is as shown in the figure 4.2.1. The light from the light source is focused and enters the monochromator. It is dispersed by the grating in the monochromator and focused on exit slit. The light that passes through the exit slit is monochromated. This light is split into two beams by a sector mirror, one going to the sample to be measured and the other to
the reference sample. The beams that have passed through the sample and reference sample are
alternatively incident upon the detector. The computer collects the data and the spectrum is
obtained.
Chapter 5

5.1. Results and Discussion

5.1.1. Fabrication of Opal Photonic crystal of Poly styrene spheres by Vertical Deposition Method.

Thin film artificial opals were fabricated by the vertical deposition method as described in section (3.1) by taking an aqueous suspension of polystyrene spheres having diameter 220nm, supplied by M/s. Duke Scientific Corporation U K. 10ml aqueous solution of Polystyrene particles with 0.25wt% is used for making the opal photonic crystal. The crystal growth process was carried out on a quartz slide (dimension 4cm×0.9cm×1mm) properly cleaned with alcohol and Milli-Q water. The slide was vertically dipped into a cylindrical vial (diameter of 1cm and height of 3cm) containing polystyrene suspension. The colloidal suspension along with the substrate was kept for uniform heating at 40^\circ C for 48 hours. In this case polystyrene particles was deposited in a small area on the bottom side of the quartz slide.

It is found that when the substrate was dipped vertically inside the vial containing the polystyrene suspension, the quality of deposition was observed to be poor, but when the substrate was kept at an angle of slightly greater than 20^\circ, the quality of the polystyrene opal formed was found to be good, which is because of the decrease in the meniscus angle [25].

Fig 5.1 shows the photograph of polystyrene opal photonic crystal formed on a quartz slide substrate, which showed strong light green iridescence under white light illumination due to diffraction of light by ordered polystyrene sphere planes. The presence of crystalline ordering of polystyrene spheres of diameter 220nm was observed. The opal film however shows few streaks. This is due to the experimental artifact (inhomogeneity of the evaporation rate of water because of temperature fluctuation, but their presence does not alter the optical and structural properties.
Fig 5.1. Photograph of Polystyrene opal photonic crystal showing green iridescence.

5.1.2. Atomic Force Microscopy

The structural characterization of the photonic crystals fabricated by the vertical self-assembling method was done using atomic force microscope (AFM) in tapping mode. Figure 5.2(a) shows the AFM topographic image of the opal structure made with polystyrene spheres of diameter 220nm. Fig. 5.2(a) shows the (111) plane of the close packed FCC structure being formed parallel to the substrate with hexagonal ordering. Figure 5.2(b) shows the opal structure made of multiple layers of 220nm polystyrene particles.
Fig 5.2 (a) AFM image of opal photonic crystal made from 220nm polystyrene which shows the view of (111) plane of the crystal. (b) AFM image showing multiple layers of photonic crystal made from 220nm polystyrene.

5.1.3. Crystalline Order and Pair Correlation Function

The pair correlation function is given by the equation

\[
g(r) = \frac{1}{\rho} \left( \sum_{j \neq i} \delta(r_i - r_j - r) \right)
\]

Where \( \rho \) are the average number density and the indices \( i \) and \( j \) run over all the particles.

The AFM images obtained were processed and analyzed using Leica QWIN software for obtaining the particle coordinates (x, y). Using these coordinates the in-plane pair correlation function (two dimensional \( g(r) \)) is computed by a FORTRAN program with input parameters such as number of particles, number of frames, image dimensions and particle diameter.

In plane pair correlation function gives the probability of finding a particle at a distance \( r \) and \( r + dr \), given a particle at the origin (21). It is essentially the ratio of the number of particles \( n(r) \) at distance \( r \) from the origin in the neighbourhood of \( r \) and \( r + dr \) to average area density, \( \rho \) of the system, i.e.
\[ g(r) = \frac{n(r)}{2\pi \rho r} \]

\( g(r) \) is used to characterize the structural ordering of the particles in the plane. It can be used to quantify the quality of particle ordering. From the \( g(r) \), lattice constant is also calculated.

The calculated 2D \( g(r) \) patterns for a single crystalline layer of polystyrene opal showing hexagonal order is shown in Fig. 5.4. The peaks in the \( g(r) \) are consistent with that of hexagonal arrangement of particles in the layer. In \( g(r) \) the first peak corresponds to the nearest neighbor distance \( d_{nn} \). In this case, \( d_{nn} \) occurs at 317nm.

Fig 5.3. Two dimensional pair correlation function of top layer of a photonic crystal made from 220nm polystyrene particles.
5.1.2. Optical Characterization of PS opal photonic crystal.

5.1.2.1. Reflection Spectra.

Reflection spectra analysis is the efficient and best method for studying the band gap of photonic crystals and their quality. In the case of photonic crystal the reflection peak is due to Bragg reflection of the waves reflected from family of parallel planes inside the photonic crystal. Reflection spectra from polystyrene opal photonic crystal are investigated using a Jasco V 650 spectrophotometer. The reflection spectrum was taken from the (111) plane of the crystal, which is the densely packed surface plane of the crystal, parallel to the substrate at normal incidence. Since the lattice constant of PS opal photonic crystal is in visible region, it will show a reflection peak in the visible region due to Bragg diffraction. The opal photonic crystal made from 220nm polystyrene shows reflection peak at 516.5nm. Fig 5.6. shows the reflection spectra for fcc (111) plane of the opal photonic crystal fabricated with 220nm polystyrene with a size distribution of 1.6%.
Fig 5.4. Reflection spectra of 220nm Polystyrene opal photonic crystal.

The position of reflection peak for an FCC photonic crystal can be estimated using a modified form of Bragg’s law which takes into accounts the refraction of light in the periodic structure and the incident angle of the incoming light, which is given by the equation

\[ \lambda = 2d_{111} \times \sqrt{(n_{\text{eff}}^2 - \sin^2 \theta)} \]

where \( \lambda \) is the wavelength of the reflected peak

\( d_{111} \) is the interplanar spacing of the closed packed (111) planes given by \( d_{111} = 0.816 \times D \), where D is the diameter of the PS spheres The polystyrene colloidal crystal film shows fcc arrangements of spheres, with their fcc (111) planes parallel to the quartz substrate.

\[ d_{111} = 0.816 \times 220\text{nm} = 179.5\text{nm} \]

\( n_{\text{eff}} \) is the effective refractive index. The average effective refractive index of the structure is related to the volume fractions of PS and that can be obtained from equation

\[ n_{\text{eff}} = n_{\text{sphere}} \times f + n_{\text{void}} (1-f), \]

where \( f \) is the filling fraction of the sphere. Filling fraction of 0.74 is expected for a fcc arrangement of solid spheres, thus \( n_{\text{eff}} = 1.59 \times 0.74 + 1(1-0.74) = 1.4366 \), refractive index of PS spheres being 1.59.

\( \theta \) is the angle of incidence of light on the sample with normal along the [111] direction, which is 0° for our experimental condition. Hence the approximate wavelength at which reflection is expected is given by using eq.5.2.

\[ \lambda = 2 \times 179.52 \times 1.4366 = 515.79\text{nm} \]

The measured wavelength peak from the reflectance spectra i.e. clearly obeys the modified Bragg’s law expression given in equation 5.2. From equation 5.3, it is clear that the peak wavelength of reflection of the photonic crystal depends upon the refractive index of the material of the sphere, the diameter of the sphere used for fabrication of photonic crystal and the angle of
incidence of light. Thus by selecting these parameters the position of the stop band in the photonic crystal can be controlled.

The reflectance is measured over multiple areas of the sample and the wavelength of the peak reflectance is found to vary within 1.8% over different domains of the sample which is an indication of the extent of ordering in the photonic crystal. The refractive index of the material of the sphere and that of the voids decide the value of the effective refractive index and in turn the value of the effective refractive index and diameter of the PS sphere decides the stop band wavelength region. Hence by selecting a suitable sphere diameter and filling the voids with a material of different refractive index, one can change the value of $n_{\text{eff}}$ and thus can tune the photonic stop band.

5.1.2.2. Band structure of Opal PS photonic crystal

The band structure of an ideal fcc photonic crystal is calculated using a freely available software package “MPB”(developed by the peoples at MIT), which uses the plane wave expansion method for the calculation of band structure. Inputs needed for calculating the band structure are as follows:

Lattice constant: $a = \sqrt{2} \times D$, where D is the sphere diameter. In our case $a$ is 311.13nm

Radius of the sphere in terms of lattice constant, $r = 0.35355a$

k points inside the crystal, this is the set symmetry points at the edges of fcc within the first Brillion zone. Symmetry point coordinates for the reciprocal lattice is represented in figure 5.5 are
Fig 5.5. Symmetry points in the Brillouin zone edges (Taken from Ref. [22])

\[
\begin{align*}
X &= (0, \frac{1}{2}, \frac{1}{2}) \\
U &= (0, \frac{5}{8}, \frac{3}{8}) \\
L &= (0, \frac{1}{2}, 0) \\
W &= ((\frac{1}{4}, \frac{3}{4}, \frac{1}{2}) \\
K &= ((\frac{3}{8}, \frac{3}{4}, \frac{3}{8}) \text{ and } \Gamma = (0, 0, 0)
\end{align*}
\]

Dielectric constant of the spheres: For polystyrene dielectric constant is 2.5281, and the void is air having dielectric constant 1

Figure 5.6 shows the 3D band diagram of opal Polystyrene photonic crystal for first Brillouin zone of the photonic crystal. Actually this band diagram gives the optical characteristics of the entire photonic crystal due to the periodicity of the crystal lattice. X axis represents the wave vectors, which is spanned for first Brillouin zone with it’s highly symmetry points. This highly symmetry points are represented with Γ, X, L etc. The magnitude of those vectors is represented in the X axis. Y axis represents the frequency of the wave inside the first Brillouin
zone of the photonic crystal. Frequencies are calculated in units of c/a, where c is the velocity of light in vacuum and ‘a’ is lattice constant of the crystal. Photonic crystal made from 220nm polystyrene spheres having lattice constant of 311.1. The number of bands calculated is 11.

The band diagram shows a pseudo gap at 0.55c/a = 0.55×3×10^8/311.1×10^9 = 5.302×10^{14}Hz., which corresponds to a wavelength of 565nm. This photonic band gap is in (Γ-L) direction which corresponds to the [111] direction in the FCC photonic crystal. The measured reflection peak from UV –Visible is at 516.47nm. The stop band calculated from the band structure is little higher than the stop band measured from UV-Visible. The calculation is done with an ideal fcc arrangement while the prepared sample is likely to have a few inherent defects due to the self-assembly process. There will be a certain amount of inhomogeneous broadening in the reflectance peak due to these defects in the structure [19]. Any anomaly in the stacking of the multiple layers will lead to lowered reflectance values. As mentioned in section 5.1.2.1, the measured gap wavelength values have a standard deviation of 1.8% when the data is obtained from multiple areas of the same sample. When this is taken into account, the discrepancy between the measured and calculated values is within the expected limits.
Fig 5.6. Band diagram of PS opal photonic crystal plotted using MPB software
Chapter 6

6.1. Conclusions

Polystyrene opal photonic crystals of good quality were fabricated using simple and efficient vertical deposition method. During this process, polystyrene spheres are organized in a face centered cubic (fcc) structure due to the capillary force that exist in the meniscus between the substrate and the colloidal particle. Good deposition of PS spheres was observed when the substrate was inclined at an angle slightly greater than $20^0$ with respect to the vertical of the vial, which is due to lowering of the meniscus angle near the substrate. Photonic crystal showed a strong light green opalescence under white light illumination due to diffraction of electromagnetic waves from (111) planes. The structural characterization of the photonic crystals fabricated by the vertical self-assembling method was done using atomic force microscope (AFM). AFM characterization revealed the long range crystalline order of the photonic crystal, with hexagonal ordering.

Reflectance measurements were done for characterizing the quality and stop band of the photonic crystals. The position of the reflection peak of the photonic crystal is calculated using modified form of Bragg’s law (equation 5.3) and found to be 515.79 nm. The Reflection spectra of the photonic crystal made from 220nm polystyrene sphere measured using UV Visible spectrophotometer showed the reflection peak at 517nm The measured reflectance peak wavelength shows a good resemblance with the calculated one using modified form of Braggs law. The refractive index of the material of the sphere and that of the voids decide the value of the effective refractive index and in turn the value of the effective refractive index and diameter of the PS sphere decides the stop band wavelength region. Hence by selecting a suitable sphere diameter and filling the voids with a material of different refractive index, one can change the value of $n_{eff}$ and thus can tune the photonic stop band.

The band structure for the opal photonic crystal fabricated with 220nm PS spheres is calculated with MPB photonic band gap calculating software developed at MIT. A pseudo gap is observed in $\Gamma$-L direction at 0.5c/a which corresponds to a wavelength of 565nm. The
wavelength corresponds to pseudo gap is in green region of electromagnetic spectrum. The stop band calculated from the band structure is little higher than the stop band measured from UV-Visible. The calculation is done with an ideal fcc arrangement while the prepared sample is likely to have a few inherent defects due to the self-assembly process. There will be a certain amount of inhomogeneous broadening in the reflectance peak due to these defects in the structure. Any anomaly in the stacking of the multiple layers will lead to lowered reflectance values.
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