COMPUTATIONAL STUDIES OF ENGINEERED DEFECTS
IN COLLOIDAL PHOTONIC CRYSTALS

by

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Abstract

This thesis is an exploration of the properties of engineered defects in self-assembled photonic crystals, with particular attention paid to the complete band gap of the a-Si inverse opal. The potential of this metamaterial for optical signal processing in telecommunications is studied using a pair of complementary simulation techniques; one is a frequency-domain code, while the other is in the time domain. Calculations of photonic states associated with isolated point defects are performed, and their cavity modes, losses and field distributions are calculated. The equivalence of two classes of defects is demonstrated, and a robust, single-mode point defect microcavity is proposed. A linear defect waveguide, comprised of coupled chain of such point defects, is analyzed. Transmission around sharp bends is demonstrated, and some simple devices are considered. Several potential approaches to fabrication of the defects, the properties of various candidate materials, and more complex devices are discussed.
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This thesis is the result of many hours of calculations carried out on a variety of computer systems; however, the bulk of the simulations were carried out on the Bigmac cluster in the U of T Physics department, so I would like to especially thank Leslie Groer and Greg Wu of Physics for generously supplying me with an account and their unused clock cycles. The theoretical work in this paper represents a portion of a larger and more comprehensive project aimed at designing, constructing and testing opal-based photonic devices. I would like to thank the following people from around the University for their assistance with the experimental end of this project: Henry Lee from ECTI for his assistance with photolithography and clean room processing, Sal Boccia from MSE for his help in setting up and troubleshooting the Zyvex system, Venkat Venkataramanan of the IOS for assistance with laser holography, Ilya Gourevich of the CNI, for his assistance with microscopy, and especially Sue Mamiche for doing everything and making the trains run on time.

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Chapter 1
Introduction

1.1 – Motivations for Engineered Defects in Photonic Crystals

Modern society has benefited greatly from the application of semiconductor physics to the microelectronics industry. Since the development of the transistor in the 1950s, the west has seen unprecedented growth in terms of economic output and standard of living, due in large part to the advent of cheap, small, and powerful microprocessors. Our hunger for ever more computing power seems boundless; as the electronics have become smaller and faster, they have also become nearly ubiquitous in modern life.

The smaller the circuit, in general, the faster it runs. As feature sizes have shrunk to a few tens of nanometers, however, some fundamental limitations on the nature of semiconductor-based electronics have become apparent. A valiant effort by chip designers to sidestep these issues has allowed the microprocessor industry to continue to grow, but a massive search is underway for a wholly new platform, one that will overcome these issues.

A number of potential technologies are being explored as possible replacements for current semiconductor technology. In general, the problem is one of transmitting and manipulating information carried by some physical mechanism. Some of the more prominent efforts involve the studies of encoding this information in electronic spin states (spintronics), optical pulses in monolithically fabricated optical circuits (integrated optics), and charge transport across single molecules (so-called single molecule electronics). The subject of this thesis is a variation on the integrated optics approach, using photonic crystals as a platform for transporting and manipulating light.

1.1.1 – The Limitations of Semiconductor-based Electronics

Modern integrated circuits are generally fabricated via photo- or electron-beam lithography, on single-crystal silicon wafers. Multiple steps of masking, etching and redeposition are employed to build up multi-level structures. Smaller features means more computing power can be packed into a given area. The steady progress in shrinking these features was recognized in 1965 by Gordon Moore, then an engineer at Intel. Since that time, the average number of transistors per
unit area has roughly doubled every 18 months, a trend now called Moore’s Law\(^1\). This trend has fueled the growth of the computer and telecommunications industries.

The cutting edge in deep UV photolithography involves feature sizes of 45 nm, which allows for an extraordinarily high component density, short switching times and billions of calculations per second. As feature sizes shrink and transistor densities grow, a number of issues will become problematic. One such problem is that as electrons are confined to dimensions approaching their de Broglie wavelength (which, in silicon, is \(\sim 10\) nm), the conduction-band energy levels available to them become widely spaced. These so-called quantum size effects will require a radical rethinking of electronics design. Furthermore, the atomic nature of matter presents an ultimate limit to the size of electronics. The trend in feature sizes is shown in Figure 1.1.

![Figure 1.1 – Long term trends in commercially available CPU MOSFET dimensions\(^2\), with extrapolated fit. At the current rate, the transistor gate length will approach the de Broglie wavelength of electrons in Si in 10 years, and the atomic length scale within 30 years.](image)

Other technological problems have already warranted a change in the direction of microprocessor development. After years of growth, CPU core clock speeds have been limited to roughly 4 GHz (Figure 1.2a). There is no single technological reason for this shift\(^3\). One is simply power density: high switching rate means high switching current, and coupled with a high transistor density, modern CPUs now generate resistive losses of several hundred watts
per cm$^2$. The management of this waste heat is non-trivial, as anyone who has ever used a modern laptop on their lap will know. The RC time constant of the on-chip interconnects between transistors and the delay associated with accessing RAM (now several hundreds of clock cycles) also have conspired to limit the clock speed.

Industrial microprocessor designers have attempted to sidestep these types of problems by employing a number of clever techniques such as pipelining, predictive decision-making, and parallel designs, with up to 8 cores per CPU now commercially available. While these efforts have continued to increase the computational output of a given processor (Figure 1.2b), it is clear to many that these are stopgap measures, and that the fundamental physics of semiconductor circuitry will not allow for indefinitely continued progress.

Figure 1.2 – Long-term trends in CPU clock speeds (left) and instructions per second (right)$^4$. The roughly linear growth (black line) has saturated near 4 GHz (red line), mainly due to thermal problems associated with extremely high transistor densities. Advances in CPU design, notably parallelization, have allowed for continued growth despite this limitation.

1.1.2 – Optical Solutions

The use of optical signals to transmit data has grown tremendously since the 1970s, when the telecommunications industry began switching from copper conductors to fiber-optic transmission lines. Communicating with photons instead of electrons has a number of advantages. First, while there are losses in fiber optics due to scattering and absorption, the problems of thermal management associated with resistive heating are a non-issue.
Furthermore, in linear materials the superposition of Maxwell’s equations allows multiple signals to be transmitted independently at different frequencies, which could allow for simultaneous processing at multiple wavelengths.

Optical fibers rely on the phenomenon of total internal reflection (TIR), whereby the light is transmitted through a core of high refractive index, surrounded by a low-index cladding layer. TIR has been in recent years exploited to guide light along small waveguides defined on a chip by lithographic means. This monolithic integrated optics approach has been successfully used to fabricate working waveguides, splitters, filters, switches and other component-level devices which could be used in an optical microprocessor. However, the nature of the internal reflection confinement requires that bends be gradual; there is a fundamental trade-off between the radius of a waveguide bend and the fraction of light lost due to scattering (see Figure 1.3). Despite the use of active media for wave guiding and clever design, there is a limit to the degree of miniaturization achievable with these devices.

![Figure 1.3](image.png)

Figure 1.3 – Calculated bend losses as a function of radius of curvature in an integrated optical waveguide. The vertical axis is losses in units of dB/cm. Sharp bends on the order of ~1 μm have enormous losses.
1.1.3 – Photonic Crystals as a Platform for Optical Computing

Photonic crystals are a class of materials whose defining feature is a periodic variation in the dielectric constant. This periodicity can be one-, two- or three-dimensional. The case of one-dimensional photonic crystals, so-called distributed Bragg reflectors (DBRs), has been understood for quite some time. A well-manufactured thin film DBR can have reflectivity approaching 100%, for a range of wavelengths which are roughly the length scale of the film’s periodicity. This range is called the photonic band gap (PBG).

It was in 1987 that Yablonovitch and John independently discovered that a dielectric material manufactured with three-dimensional periodicity could exhibit a band gap that spanned all possible spatial directions. This complete photonic band gap, a range of wavelengths which are forbidden to propagate in any direction in the material, has become the subject of intense study, both for its fundamental physics and for a vast number of promising applications.

Much of the early experimental work on photonic crystals was carried out with dielectrics structured at a centimeter length scale (and therefore exhibiting a band gap in the microwave wavelengths). However, the size invariance of Maxwell’s equations allows the scaling to shorter (or longer) wavelengths simply by scaling the dielectric structure accordingly, so long as the materials in use remain close enough to ideal, linear dielectrics. While no photonic crystal has yet been made that exhibits a complete band gap in the visible spectrum, the high refractive index of a number of semiconductors in the near infrared has been used to fabricate a number of structures with a complete band gap at the 1.55 μm telecommunications wavelength.

It is believed that defects in a photonic crystal exhibiting a complete band gap can be used to trap and manipulate light, allowing one to design waveguides, bends, splitters, and other devices. The nature of the confinement is fundamentally different from that of total internal reflection, allowing for the sharp bends that are necessary for miniaturization and integration into a microchip-scale processor.

It is to the problem of design that we now turn. The system under study will be the silicon inverse opal, a self-assembled three-dimensional photonic crystal. The inverse opal exhibits a complete band gap between the 8th and 9th bands. By scaling the structure appropriately, the complete PBG can be made to coincide with the 1.55 μm telecom window. In this thesis, I will explore the optical properties of various point and linear defects in a silicon inverse opal. The focus will be on the strong confinement due to the complete band gap, with an aim to engineer defect structures for efficient light trapping and guiding.
1.2 – Photonic Crystals

1.2.1 – One and Two-dimensional Photonic Crystals

One-dimensional photonic crystals, known variously as DBRs, dielectric mirrors or quarter-wave stacks, have been studied and understood for quite some time. The latter name comes as an extension of the concept of the quarter-wave thin film antireflection coating, where a low-index coating of thickness $\lambda/4$ can be used to reduce the reflectance of an optical element to nearly zero. This effect may be understood as destructive interference of waves reflected from the front and rear surfaces of the coating. On the other hand, a high-index film will result in increased reflectance, due to a 180 degree phase shift on reflection at the back of the film. A stack of alternating high and low index layers can approach 100% reflectance for a range of wavelengths around $\lambda$. This range is roughly equal to the periodicity of the stack, and represents the photonic band gap of the one-dimensional structure.

As the periodicity is increased to more dimensions, the novel and useful properties of photonic crystals become apparent. An example of a two-dimensional PC is a lattice of infinitely long dielectric rods in air. The formation of a PBG is again observed, this time in the direction perpendicular to the rods. This type of structure has been studied extensively both in theory and experiment. A number of designs for waveguides and various PC devices have been considered, typically as a lattice of holes in a high-index film, with a row of missing (or otherwise modified) holes defining a linear defect that can guide light. In the plane of the film, confinement is achieved by the PBG, and in the out-of-plane direction, by total internal reflection at the interface between the film and the surrounding cladding material. This vertical confinement is somewhat lossy, but allows for easy coupling of light into and out of the structure.

1.2.2 – Three-dimensional Photonic Crystals

Complete confinement of light to a defect may be realized by increasing the periodicity of the structure to three dimensions. In this case, the PBG may span all directions in space, giving rise to a situation where no propagating modes exist for a range of frequencies in any direction. A number of structures exhibiting this property in various regions of the spectrum have been fabricated and quite a few more have been theoretically studied. One structure, the so-called “woodpile,” is made up of rows of rods stacked in an alternating x-y-x-y fashion, offset such that the rod crossings share the tetragonal symmetry of the diamond crystal structure. When
fabricated from a material of high refractive index such as Si, the woodpile structure can be made to have a complete PBG. Other 3D photonic crystals have been made at a variety of length scales and using a variety of techniques; these include lattices of intersecting rods\textsuperscript{12}, quasicrystalline structures,\textsuperscript{13} and various structures made by laser holography\textsuperscript{14}.

![Figure 1.4 – Scanning Electron Micrograph of a synthetic opal.](image)

1.2.3 – Opals and Inverse Opals

Nature provides us with her own photonic crystal, the precious gemstone known as opal. Viewed at high magnification, opals are seen to be made up of a regular three-dimensional array of sub-micron silica spheres, arranged in a close-packed structure. Opalescence – the shifting colors observed when looking at an opal in white light – is a result of the reflection of different wavelengths from various crystal planes. This reflection is due to the incomplete band gap of the silica opal. This is the situation where certain directions of high symmetry exhibit a partial band gap, but it does not extend across all directions.

However, an opal may be transformed into a material with a complete photonic band gap by the process of inversion. In this process, the interstices between the spheres are filled with a high-index material, and the spheres themselves are subsequently removed by heating or etching. The result is essentially a three-dimensional negative of the original opal structure, and is called
an inverse opal. The inverse opal does exhibit a complete band gap when the refractive index of the material used in the inversion is greater than 2.85\(^{15}\).

Synthetic thin film inverse opals can be made in the laboratory with very high quality. There are three main steps involved in the fabrication of an inverse opal. First, a dispersion of colloidal microspheres is synthesized. These spheres are allowed to self-assemble onto a substrate, and then the high-index material is deposited in the pores between the spheres. Finally the template spheres are removed and what remains is an inverse opal. In Chapter 2, I will describe in further detail the steps involved in fabricating an a-Si inverse opal made from a template of silica microspheres.

1.3 – Defects in Opals and Inverse Opals

The presence of defects in photonic crystals is both a curse and a boon. Though rapid advances in atomic crystal growth have resulted in near-flawless crystalline wafers, no real-world crystal is truly perfect. This is also true of colloidal crystals, which exhibit various flavors of defects that are roughly analogous to the defects found in atomic crystals. These include inclusions, vacancies, stacking faults, dislocations, grain boundaries and cracks. These defects are illustrated and summarized in Table 1.1.

While most of these defects disrupt the long-range order of the crystal and therefore compromise its photonic properties, some do not, and these can be exploited and engineered to have useful properties. This is the essential focus of this thesis – engineering the optical properties of a subset of these defect types to trap and guide light within an inverse silicon opal.

1.3.1 – Point Defects

In this thesis I will focus specifically on point defects. These are defects such as inclusions or vacancies in the crystal lattice which are a disruption of the ideal crystal structure at the location of a single lattice point. A typical example might be an off-size microsphere, or one of a different material than the bulk crystal. In analogy to the inclusions found in semiconductor crystals, where defect atoms can act as traps for electrons or holes, a point defect in a photonic crystal can localize photons via confinement by the complete PBG. At the location of the defect, the crystal symmetry is broken and localized defect states are formed.
Table 1.1 – Survey of various intrinsic colloidal crystal defects. (1) and (2) are non-point defects, while the inclusion of an oversized sphere (3) must lead to a dislocation. These contribute to long-range disorder in the crystal, while interstitial (4) and substitutional inclusions (5) and (6) are localized, and may be considered point-like.

By properly adjusting the properties of the defect such as its geometry or refractive index, the states can be made to lie at frequencies inside the PBG resulting in trapped light. An individual point defect can thus act as a microscopic cavity; these resonators can have extremely large quality factors and therefore extend the cavity photon lifetime far beyond normal levels. Such a resonator might serve as a short-term memory cell in a photonic computer, or allow for studies of light-matter interaction over time scales that have been previously inaccessible.

Since those defects which disrupt the long-range order of the crystal are not really point-like in nature, I will limit the study to those types of defects which are “atomic” in nature, in that they can be localized to a single lattice point. These are the type I and type II substitutional defects listed in Table 1.1. A type I defect is one formed when a normal lattice sphere is removed and replaced with a smaller one. A type II defect is similar, but the removed sphere is replaced with
a different material which has a different index of refraction. These two classes will form the basis of my study of point defects.

1.3.2 – Linear Defects

A row of point defects in a photonic crystal may be viewed in two ways – as a single linear defect, or as a collection of coupled point defects. The choice in how to treat such a structure depends on the strength of the coupling between those defects, which is in general a function of their spatial separation, defect geometry, and so on. Such a linear defect can act as a waveguide, essentially a “wire” in a photonic crystal processor along which signals are routed to various devices. The design of this kind of waveguide should include bends and junctions for splitting and recombining optical signals.

1.3.3 – Functional Materials as Photonic Crystal Defects

Beyond these simple structural defects, much of the potential utility of devices in photonic crystals involves the incorporation of novel materials into the structure. There is a wide variety of active and nonlinear materials which depart from the simple dielectric model used in most of this work. Incorporating these materials into a PC lattice may allow for highly functional photonic crystal devices.

One example is electro-optic materials, which exhibit a change in refractive index due to an applied electric field that may be linear (Pockels effect) or quadratic (Kerr effect) in the field magnitude. There are a broad range of materials which exhibit these properties, including inorganic crystals like KTiOPO₄ or LiNbO₃, electrically poled polymers, or even liquids like nitrobenzene. If these materials are introduced as defects into the photonic crystal lattice, they could enable switching or modulation of the light intensity along a waveguide.

Luminescent materials such as fluorescent dyes or nanocrystal quantum dots, when introduced into a microcavity point defect, could serve as a gain medium in a microlaser for signal amplification. The output of such a microlaser critically depends on the frequencies of the defect modes present in the cavity. Other, more exotic effects (acousto-optics, birefringence, Faraday rotation, and so on) could be conceivably exploited as well.
1.4 – Overview of the Thesis

This study is essentially a theoretical exploration of the mutual interaction of the complete photonic band gap of the silicon inverse opal, point defects in the opal structure, and light at frequencies within the band gap. The real-life complications arising from the materials chemistry of this material, and departures from the ideal dielectric are considered, in order to have a more complete understanding of the potential of these devices. Two computational algorithms – one in the frequency domain, one in the time domain – will be used in a complementary fashion to study how light can be confined to defects in an inverse opal.

1.4.1 – The Plane-wave Expansion and FDTD Techniques

The two main simulation techniques employed in this thesis are the plane-wave expansion (PWE) and finite-difference time domain (FDTD) simulations. In the plane wave expansion approach, an infinite crystal is assumed. By the Bloch theorem, Maxwell’s equations may be expressed as an eigenvalue-eigenvector problem and expanded as a Fourier summation of plane electromagnetic waves. The number of terms in the expansion is truncated to a finite number, and the solution is arrived at by standard matrix diagonalization techniques. The resulting eigenvalues can be plotted versus the wave vector to arrive at a dispersion diagram for the infinite crystal, known as a band structure. The eigenvectors describe the field distribution in the crystal and can also be plotted to show the field distribution in the crystal.

The FDTD approach is a general time-domain technique for the approximate solution of Maxwell’s equations. A simulation region is defined with appropriate boundary conditions, along with the objects and their material properties, as well as any sources of radiation. Maxwell’s equations are discretized by replacing the infinitesimal quantities such as dx, dy, etc., by finite quantities Δx, Δy, etc., and the simulation volume is divided into a fine grid of computational cells. In each cell, the discretized Maxwell’s equations are solved at a time $t_0$, and the resulting solution is used as the initial condition for the next time step $t_0 + \Delta t$. The accuracy of the approximate solution arrived at in this manner is limited only by the size of the time step and grid cells, which is in turn limited by the computational power available for the simulation.
1.4.2 – Thesis Outline

In Chapter 2, I will describe in more detail the two computational techniques used, as well as give background on the synthesis, structure and properties of the colloidal photonic crystals studied. Computational studies of single, isolated point defects – their mode structure, frequency, quality factor, and so on – will be described in Chapter 3. Chapter 4 will concern the study of how light can couple between adjacent defects, and be guided along rows of point defects. Finally, in Chapter 5, I will discuss some of the challenges and materials aspects of these structures, including potential approaches to fabricating these structures on the length scale of visible and near infrared radiation.
Chapter 2
Methods

In this chapter I will outline the structure and material properties of the a-silicon inverse opal, give details on the constraints on device design imposed by the self-assembled nature of the photonic crystals under study, and describe in detail the two main simulation techniques used in this thesis.

2.1 – Inverse Opal Fabrication

A discussion of the typical steps involved in the fabrication of the Si inverse opal will inform some of the constraints placed upon engineered defects in the structure. The typical approach follows three major steps: the chemical synthesis of colloidal silica microspheres, their self-assembly into a colloidal crystal, and finally the inversion with silicon.

2.1.1 – Stöber Synthesis of Colloidal Silica

For the synthesis of silica microspheres, the Stöber process\textsuperscript{16} or some derivative thereof is the most widely used. An alcohol (typically ethanol) is mixed with a base (typically NH\textsubscript{3}OH) and a small amount of water. Under stirring, a silicon alkoxide (typically tetraethoxysilane, TEOS) is injected to the mixture. The base catalyzes the hydrolysis of the alkoxide:

\[
Si(\text{EtO})_4 + 2H_2O \Rightarrow SiO_2 + 4\text{EtOH} \tag{2.1}
\]

resulting in the spontaneous nucleation and growth of silica nanoparticles. As the reaction proceeds, these nanoparticles homogeneously agglomerate into spherical colloidal particles of porous silica, with diameters ranging from roughly 20 nm to 2 \(\mu\)m, depending on the initial concentrations of the reactants. With appropriate control of the reaction conditions (temperature, stirring speed, etc.), the final particles can have a polydispersity as low as one to two percent\textsuperscript{17}, measured as standard deviation about the mean diameter. Due to the porosity,
the refractive index of the spheres in question is considerably lower than that of bulk SiO₂. The process is illustrated in Figure 2.1.

![Diagram of the Stöber process for synthesizing colloidal silica. TEOS is hydrolyzed to form silica nanoclusters. These clusters agglomerate into larger particles, which grow uniformly into spherical particles.](image)

Figure 2.1 – The Stöber process for synthesizing colloidal silica. TEOS is hydrolyzed to form silica nanoclusters. These clusters agglomerate into larger particles, which grow uniformly into spherical particles.

2.1.2 – Evaporation-induced Self-assembly

After purifying the colloidal dispersion, a thin-film opal is grown using a technique known as evaporation-induced self-assembly\(^8\). A flat substrate, typically a glass slide or Si wafer, is cleaned and hydrophilized in Piranha solution, and then suspended vertically in a vial of the colloidal solution. Mass transport of the solvent during evaporation drives the particles upwards towards the meniscus, where they are deposited on the substrate. As the solvent dries, capillary forces between individual particles pull them together into a close-packed
structure. The number of layers deposited is a function of the size of the microspheres and their concentration, and the deposition can be controlled to result in anywhere from one to approximately 15 layers. This process can be repeated to form high-quality films of up to 50 layers in thickness.

2.1.3 – a-Silicon Inversion

The final inversion step involves deposition of the high-index material and removal of the silica microspheres. For silicon inverse opals, this can be done by vapor deposition techniques such as CVD\textsuperscript{19}. The opal film is mounted on a heating element inside a vacuum chamber. The chamber is evacuated and the sample is heated to approximately 350° C. Disilane gas (Si\textsubscript{2}H\textsubscript{6}) is introduced at low pressure, and at the hot surface of the opal it decomposes into amorphous silicon and H\textsubscript{2} gas. The deposited silicon coats the microspheres in a conformal fashion, until the interstitial openings are blocked and the precursor gas can no longer penetrate into the pores. The silicon/silica composite structure is then removed and placed in a dilute aqueous HF solution, which dissolves the silica. The resulting structure is the a-Si inverse opal. There is a wide variety of chemical techniques for fabricating an inverse opal of other materials based on a variety of liquid- and gas-phase chemical processes\textsuperscript{20}. The film growth, deposition and inversion are illustrated in Figure 2.2.

Figure 2.2 – Steps in the fabrication of a silicon inverse opal. Evaporation-induced self assembly (left) results in a close-packed film of silica spheres on a substrate. High-temperature chemical vapor deposition of Si\textsubscript{2}H\textsubscript{6} (middle) results in a silica-silicon composite film. Chemical etching with dilute hydrofluoric acid removes the silica spheres, leaving air voids in a network of a-Si.
2.2 – The Structure of Inverse Opals

There are a wide variety of techniques for the growth of colloidal crystals, including gravitational sedimentation, Langmuir-Blodgett\textsuperscript{21}, electrophoretic deposition\textsuperscript{22}, and numerous others. Generally, all of these methods form a crystal with a close-packed structure, where planes of hexagonal symmetry are stacked on top of each other. The most common form of close packing is the face-centered cubic (FCC) structure, in which the unit cell has a sphere at each of the 8 vertices, as well as in the center of each of the cube faces. The hexagonal layers can be observed by fracturing the FCC unit cell along the body diagonal, as shown in Figure 2.3.

The other form of close packing is hexagonal close packing (HCP), which differs only slightly from the FCC structure in that the stacking of hexagonal planes is altered somewhat. The inverse HCP structure does have a complete photonic band gap\textsuperscript{23}, but the width of the band gap is smaller than in the FCC system. A real colloidal crystal is typically a random mixture of HCP and FCC stacking; however, since the FCC structure is the slightly more energetically favorable configuration\textsuperscript{24}, I postulate that advances in colloidal crystal growth techniques can eventually lead to the elimination of stacking faults. Since an entirely FCC colloidal crystal should be in principle within reach, I will focus on the case of FCC stacking for the rest of this thesis.

![Figure 2.3](image)

Figure 2.3 – The unit cell of the FCC crystal is replicated for clarity and cleaved along the [111] plane, revealing planes of hexagonal symmetry.

2.2.1 – Crystal Structure and Lattice Vectors

Any kind of periodic structure may be described by a primitive unit cell and the set of lattice vectors, which upon translation by any combination thereof, leave the crystal unchanged. An
example of a two-dimensional crystal with unit cell and a set of corresponding lattice vectors is shown in Figure 2.4. The choice of primitive unit cell and lattice vectors is somewhat arbitrary, but an appropriate choice can simplify calculations.

![Diagram of a two-dimensional crystal]

Figure 2.4 – A generic two-dimensional crystal (left), with unit cell outlined and lattice vectors \( a_1 \) and \( a_2 \) shown. The FCC crystal (right) can be generated by a sphere of diameter \( a/\sqrt{2} \) centered at \((0,0,0)\), reproduced over all space by repeated translations by the lattice vectors \( a_1 = (a,0,a) \), \( a_2 = (0,a,a) \), and \( a_3 = (a,a,0) \).

Each lattice vector \( a_i \) in real space has a corresponding reciprocal lattice vector \( b_j \), which are defined such that \( a_i \cdot b_j = 2\pi\delta_{ij} \) where \( \delta_{ij} \) is the Kronecker delta, equal to 1 when \( i = j \), and 0 otherwise. In reciprocal space, the smallest primitive unit cell that can be constructed is known as the irreducible (or first) Brillouin zone. The Brillouin zone of an FCC crystal is a truncated octahedron, with corners and edges that correspond to the high-symmetry directions of the crystal.

2.2.2 – The FCC Crystal

For the FCC crystal, the convention is to choose a set of lattice vectors that point from a corner sphere to each of the three nearest spheres, which lie on the face center of the cubic unit cell. These vectors, \( a_1 = (a,0,a) \), \( a_2 = (0,a,a) \), and \( a_3 = (a,a,0) \) are illustrated in Figure 2.4. For certain problems, however, an alternative choice of lattice vectors can be useful, as we shall see in Chapter 4. Directions with high symmetry, called critical points, are given a set of canonical names such as \( \Gamma, L, X \), and so on.\(^{25} \)
With most thin film deposition techniques, the resulting structure is formed with the (111) crystal plane parallel to the substrate. Patterning the substrate can allow for different orientations, but due to the difficulty of growing high-quality films in this manner, I will focus on the typical case of the (111) orientation.

2.3 – The Photonic Band Gap

All of the above language used to describe crystals comes from solid-state science, and many of the principles underlying that field can be applied to the study of photonic crystals. One example is the Bragg diffraction law, which for electron or x-ray diffraction takes the form

\[ n \lambda = 2d \sin \theta \]

A similar equation can be derived by considering the coherent scattering of light waves by the planes of the photonic crystal lattice:

\[ \lambda = 2d \sqrt{n_{\text{avg}}^2 - \sin^2 \theta} \]

where \( d \) is the interplanar spacing and \( n_{\text{avg}} \) is the average refractive index of the crystal.

Bloch’s theorem, which was first applied to the coherent scattering of electrons in semiconductors, is another example of solid-state physics repurposed to describe photonic crystals. Bloch’s theorem states that the wavefunction of an electron moving in the periodic scattering potential of a semiconductor may be rewritten as a product of a spatially harmonic plane wave with a spatially periodic function called a Bloch wave. The resulting wave equation then has discrete solutions, which gives rise to the electronic band structure of semiconductors, and all of their attendant properties.

Bloch’s theorem may be extended to photonic crystals as well, by treating light scattering by the periodic dielectric in the same manner. For this reason photonic crystals are often referred to as “semiconductors of light” in that they exhibit photonic band gaps as opposed to electronic band gaps, and can be described with similar mathematics. In the following sections, I will briefly describe the physics behind the two main tools I use in this thesis – the plane-wave expansion and FDTD algorithms – and show how the photonic band structure and other properties can be calculated.
2.4 – The Plane-wave Expansion Technique

The plane-wave expansion\textsuperscript{29} is an approach for calculating band structures for photonic crystals, by solving Maxwell’s equations in the frequency domain. The assumptions used are that the crystal is infinite and is comprised only of ideal dielectric materials. In the following sections, I will show the basic steps and describe the software used in this thesis for performing these calculations.

2.4.1 – Maxwell’s Equations for Ideal Dielectrics

In general, the behavior of electromagnetic fields is elegantly given by the Maxwell equations\textsuperscript{30}, which are in differential form (cgs units):

\begin{align*}
\nabla \cdot B &= 0 \quad (2.3a) \\
\nabla \cdot D &= 4\pi \rho \quad (2.3b) \\
\nabla \times E &= -\frac{1}{c} \frac{\partial B}{\partial t} \quad (2.3c) \\
\nabla \times H &= \frac{4\pi}{c} \mathbf{J} + \frac{1}{c} \frac{\partial D}{\partial t} \quad (2.3d)
\end{align*}

These equations, along with the constitutive relations \( \mathbf{D} = (1 + \chi_\varepsilon) \varepsilon_0 \mathbf{E} = \varepsilon \mathbf{H} \) and \( \mathbf{B} = (1 + \chi_m) \mu_0 \mathbf{H} = \mu \mathbf{H} \), are sufficient for a complete description of the general behavior of light. For our purposes, they can be simplified somewhat by making several observations. Primarily, if we restrict ourselves to \textit{linear dielectrics}, we can set the permeability \( \mu = \mu_0 \) which implies that \( \mathbf{B} = \mathbf{H} \). One can also neglect the presence of any free charges, thereby setting \( \mathbf{J} = \mathbf{0} \) and \( \rho = \mathbf{0} \).

Furthermore, since the dielectric function is explicitly a periodic function of position in space, the permittivity \( \varepsilon \) should be written with spatial dependence: \( \varepsilon = \varepsilon(r) = \varepsilon(r + \mathbf{R}) \). Here, \( \mathbf{R} \) is any vector sum of the \( \mathbf{a}_i \) lattice vectors. With these changes in place, Maxwell’s equations simplify to the more symmetric form:
\[ \nabla \cdot \mathbf{B} = 0 \quad (2.4a) \]
\[ \nabla \cdot \varepsilon(\mathbf{r}) \mathbf{E} = 4\pi \rho \quad (2.4b) \]
\[ \nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad (2.4c) \]
\[ \nabla \times \mathbf{B} = \frac{\varepsilon(\mathbf{r})}{c} \frac{\partial \mathbf{E}}{\partial t} \quad (2.4d) \]

\section*{2.4.2 – Maxwell’s Equations in the Frequency Domain}

The electric and magnetic fields \( \mathbf{E} \) and \( \mathbf{B} \) are, in general, vector quantities of the form \( \mathbf{A}(\mathbf{r}, t) \). Since we are concerned with the interaction between photonic crystals and electromagnetic waves, we can remove the time dependence by rewriting the fields as a spatially dependent term times a harmonic function in time: \( \mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}) e^{i\omega t} \). No generality is lost in doing so, as Fourier analysis allows one to describe an arbitrarily time-dependent field as a sum of harmonic waves. Rewriting \( \mathbf{E} \) and \( \mathbf{B} \) in this form and substituting into the curl equations 2.2c and 2.2d, we find:

\[ \nabla \times \mathbf{E} = -\frac{i\omega}{c} \mathbf{B}(\mathbf{r}) \quad (2.5) \]
\[ \nabla \times \mathbf{B} = \frac{i\omega \varepsilon(\mathbf{r})}{c} \mathbf{E}(\mathbf{r}) \quad (2.6) \]

The above equations may be decoupled by taking the curl of both sides and then substituting one into the other. The result is

\[ \nabla \times \left( \frac{1}{\varepsilon(\mathbf{r})} \nabla \times \mathbf{B}(\mathbf{r}) \right) = \left( \nabla \times \frac{1}{\varepsilon(\mathbf{r})} \nabla \times \right) \mathbf{B}(\mathbf{r}) = \frac{\omega^2}{c^2} \mathbf{B}(\mathbf{r}) \quad (2.7) \]
This equation for the magnetic field can be interpreted as an eigenvalue-eigenvector equation, where the operator \( \nabla \times \frac{1}{\varepsilon(r)} \nabla \times \) operates on \( B \), generating the eigenvalue \( \omega^2 / c^2 \). This eigenvalue gives the frequency of the harmonic field that satisfies this equation, and the eigenvector \( B(r) \) gives the spatial distribution of the field. Here I have done the substitution so that Equation 2.7 is in terms of the magnetic field; it would be an entirely equivalent description of the problem to rewrite it in terms of the electric field. In either case, by applying the curl equations 2.5 and 2.6 to whichever field we choose, it is possible to transform the field distribution from magnetic to electric, or vice versa. Therefore, in finding the eigenvectors of Equation 2.7, we can fully describe the electromagnetic field in the photonic crystal.

2.4.3 – Expansion of the Fields in Fourier Space

The analytical solutions to this eigenvalue problem are difficult to arrive at, so the typical approach is to expand the field \( B \) and the dielectric function \( \varepsilon(r) \) in a Fourier basis\(^{31}\). The periodicity of the dielectric structure allows for application of Bloch’s theorem and an expansion of the field in a basis set of Bloch waves:

\[
B = \sum_{G, \lambda} h_{G, \lambda} e^{i(k + G \cdot r)}
\]

Here \( \lambda \) is a dummy variable to account for both TE and TM polarizations, and \( G \) is the set of all reciprocal lattice vectors \( b_j \) corresponding to the \( a_i \) lattice vectors of the crystal. This expansion is the photonic equivalent of the solid-state physics description of electron states by Bloch waves, and it is a strict equality if the entire set of reciprocal lattice vectors corresponding to the infinite crystal is used in the summation. The dielectric function can be similarly expanded:

\[
\frac{1}{\varepsilon(r)} = \sum_{G, \lambda} K_{G, \lambda} e^{-i(G \cdot r)}
\]
Once the $\kappa_{G,\lambda}$ are known, a particular value for $k$ may be chosen, and these expressions can be plugged back into the master equation 2.7.

### 2.4.4 – Approximate solution

By truncating the above summations at some reasonable number of terms, an approximate solution can be found. Substituting the summations into Equation 2.7, a matrix equation is arrived at, where the size of the matrix is determined by how many terms in the summation are kept. This equation can be solved by standard diagonalization techniques. The solutions are the eigenvalues $\omega^2 / c^2$ corresponding to the eigenvectors (or Bloch waves) $h_{G,\lambda}$. This process is repeated over the set of $k$ vectors that trace out the edges of the first Brillouin zone of the crystal. When the frequencies are plotted vs. $k$, one arrives at a band structure such as that shown in Figure 2.5.

![Figure 2.5 – Band structure of an inverse silicon opal. The vertical axis is the normalized frequency $\varphi = 2\pi \omega / c$, where $\omega$ is calculated from the eigenvalues $\omega^2 / c^2$ of Equation 2.7. The horizontal axis is $k$, and traces a path along the edges of the first Brillouin zone. The dark gray region between approximately 0.78 and 0.82 on the vertical axis is the range of the complete band gap between the 8th and 9th bands. In the perfect crystal, there exist no modes with frequencies of this range.](image-url)
2.4.5 – The Photonic Band Structure

The band structure plotted in Figure 2.5 provides a visualization of the way that electromagnetic waves propagate inside the crystal. The horizontal axis represents directions in (reciprocal) space; the points labeled X, U, L, etc. are the critical points of high symmetry. By convention in the literature, the vertical axis is not the frequency $\omega$ but the normalized frequency $\varphi = 2\pi a \omega / c$, where $a$ is the length of the lattice vectors $a_i$. This normalization gives a scale-independent description of the photonic band structure; in other words, the band structure calculated above applies to an FCC structure of close-packed spheres of any size.

Since the band structure is a plot of frequency vs. wave vector, it can be interpreted as a dispersion relation. The value of $\varphi / |k|$ at any given point in the structure then tells us the phase velocity of the waves, while the slope $\partial \varphi / \partial |k|$ gives the group velocity. It is worth pointing out that these bands are those associated with an infinite crystal, and as such they represent photons which are extremely delocalized throughout the photonic crystal lattice.

Other important features of the band structure are the presence of a number of pseudogaps or “stop bands” like the one between 0.43 and 0.53 at the L-point. This pseudogap corresponds to the reflection peak associated with the (111) plane of the opal.

However, the most important feature for this study is the complete band gap, which for this particular crystal lies around $\varphi = 0.8 (c/a)$. Since no states exist in that range, light of those frequencies cannot propagate through the infinite crystal. Light at frequencies within the band gap that is incident on the surface of the crystal may extend somewhat into the material, but these are evanescent waves which decay in amplitude exponentially away from the surface, similar to the evanescent modes that extend beyond the interface during total internal reflection.

The presence of any local defects inside the crystal breaks the translational symmetry, thereby allowing photonic defect states to exist, confined to the area of the defect. These states can be calculated with the plane-wave expansion by specifying the unit cell to be used in the calculation as a larger block of primitive unit cells, with one modified to include a defect. This technique, called the “supercell” approach is illustrated in Figure 2.6, where a large supercell ($9 \times 9 \times 3$) of the FCC primitive unit cell is shown. Supercell calculations require many more plane waves and the resulting band structure looks very complicated due to the presence of bands folded in from outside the first Brillouin zone (see Figure 3.2). However, frequencies associated with the defect states can be calculated in this manner, as can the dispersion relation for linear defects.
The finite memory of a given computer limits the resolution of unit cell used, and therefore the numerical accuracy of the computation. The variation in the bands as a function of the number of grid points is shown in Figure 2.7. Above a resolution of 32 grid cells per direction, the bands have essentially converged. Memory constraints limit the calculation to about $48^3$ grid points per calculation; this is highly accurate for a single unit cell, but for e.g. a $3 \times 3 \times 3$ supercell, the spatial resolution is only 16 points per unit cell. At that resolution, there is some error at the higher frequencies.
2.4.6 – *MIT Photonic Bands*

The plane-wave expansion may be calculated manually, but there exist several packages designed for just this purpose which greatly simplify and expedite the calculations. The one employed in this work is called *MIT Photonic Bands*, or MPB\textsuperscript{33}. MPB was written for the calculation of photonic band structures using the plane-wave expansion method described above. MPB takes as input a description of the dielectric structure, the set of lattice vectors, and the set of $k$ vectors for which states are to be calculated. The output is the frequencies associated with each $k$, as well as the field distributions for each mode. Results from MPB will be used extensively throughout this thesis.

2.5 – The Finite-Difference Time-Domain (FDTD) Technique

FDTD\textsuperscript{34} is a flexible algorithm suited for many types of electromagnetics simulations. Whole books may be written about the topic, so I will just summarize the salient points of the algorithm here.
2.5.1 – The Maxwell Difference Equations

The approach is essentially an approximate numerical solution of Maxwell’s equations 2.3. These equations may be discretized, by replacing the differentials with deltas (hence the “finite difference” in the name – as opposed to the infinitesimal differentials of the analytical form.) Maxwell’s equations become the difference equations

\[ \nabla' \cdot \mathbf{B} = 0 \]  
\[ \nabla' \cdot \mathbf{D} = 4\pi \rho \]  
\[ \nabla' \times \mathbf{E} = -\frac{1}{c} \frac{\Delta \mathbf{B}}{\Delta t} \]  
\[ \nabla' \times \mathbf{H} = \frac{4\pi}{c} \mathbf{J} + \frac{1}{c} \frac{\Delta \mathbf{D}}{\Delta t} \]

where the standard differential \( \nabla \) operator has been replaced by a discretized version

\( \nabla' = i \frac{\Delta}{\Delta x} + j \frac{\Delta}{\Delta y} + k \frac{\Delta}{\Delta z} \). The approach is to define a simulation region in space with appropriate boundary conditions and geometry, and then to divide the region into a fine grid of points. The discretized Maxwell’s equations are solved numerically at the initial time \( t_0 \) by calculating the finite differences in the fields between neighboring cells. The time is then advanced by an amount \( \Delta t \), and the process is repeated until the fields have decayed away or a breakout condition is met. At each time step, the electromagnetic field at any point in the simulation volume may be sampled and output to a file.

2.5.2 – Limitations of the FDTD Method

The material properties of the objects within the simulation region are defined in terms of \( n \) and \( \kappa \), the real and imaginary values of the index of refraction. It is worth pointing out that, due to the time-domain nature of the FDTD calculation, any frequency-dependent behavior such as material dispersion cannot be directly simulated. Therefore, one constraint is that simulations of this kind should only be performed at frequencies far from any absorption peaks, where the dispersion is small and can be neglected. In other words, the variation in refractive index
should be small enough so that it can be treated as a constant across the frequencies being studied.

Despite this limitation, the FDTD approach is highly flexible, and in the limit of infinitesimally small grid cells and time steps, is equivalent to an exact solution of Maxwell’s equations. The numerical agreement is only limited by the computational resources available to perform the calculation. As such, arbitrarily large structures such as crystals with infinite extent cannot be exactly simulated, but with judicious use of periodic boundary conditions and the short decay length of the evanescent modes, reasonably accurate calculations can be performed.

2.5.3 – Lumerical FDTD

There are a large number of FDTD packages available, in both free and commercial forms. The package used in this study is commercial software named Lumerical FDTD. This package provides support for a number of features which are useful. These include various kinds of boundary conditions, including periodic boundaries and perfectly matched (i.e. absorbing) layers. A number of different kinds of sources can be used, including dipole radiators, plane wave sources and Gaussian sources. Material properties can also be specified in a number of ways – the complex index of refraction may be directly input, or calculated from Lorentz-Drude parameters or Sellmeier coefficients. As the simulation is run, the electromagnetic fields can be sampled at points inside the simulation volume, analyzed, and saved to disk.

2.6 – Summary

In this thesis, I will study the properties of point-like defects in inverse a-Si opals. The opals are grown on a substrate, oriented with the (111) plane of the FCC structure parallel to the substrate. Due to the planar nature of the thin films and most patterning technologies, I will constrain myself to the study of structures within a single (111) plane. These point defects will be made by replacing an air void with a smaller void – a type I substitution – or with a sphere of some material with refractive index greater than 1 – a type II substitution. All materials will be treated as ideal, linear dielectrics.

The real part of the refractive index of a-Si can vary from roughly 3.7 to 4.1 at 1.55 µm, depending on the deposition parameters. The variation in the width of the complete PBG as a function of the inverse opal’s refractive index is shown in Figure 2.8. Above about n = 4.0, the
width of the band gap changes very little, so this is about as good as the FCC inverse opal structure will get. For the sake of this study, I will use 3.9 for the index of silicon. Choosing \( n = 3.9 \), the extent of the PBG (in normalized frequency units) is from \( \varphi = 0.712 \) to \( \varphi = 0.771 \). Since these numbers are scale-invariant, we can choose a length scale to place the 1.55 \( \mu \)m light at the center of the band gap. Setting \( \varphi = 0.7415 \), we find that the sphere radius should then be 397 nm. At this length scale, the extent of the photonic band gap ranges from 1495 to 1605 nm. Since many of the calculations I perform in this thesis are done in the frequency domain, the reader will find it useful to know these numbers in units of frequency. The upper, lower, and center of the band gap are then 200.5, 186.2, and 192.9 THz, respectively.

![Figure 2.8](image)

**Figure 2.8** – Variation of the complete photonic band gap as a function of the refractive index of the inverse opal material. The red and blue lines are the maximum extent of the 8th band and the minimum extent of the 9th band, respectively. The dashed line is the gap-to-midgap ratio, a frequency-independent measure of the width of the bandgap. At \( n = 3.9 \), the gap-midgap ratio is about 7.5%.

Except where otherwise noted, I will treat the imaginary component of the index of refraction \( \kappa \) as zero, corresponding to zero absorption. This is consistent with the notion of the ideal linear and dispersion-free dielectric; however, reality is not always so kind. The extinction coefficient\(^{35} \) in amorphous silicon of light at 1.55 \( \mu \)m is roughly \( 10^3 \) cm\(^{-1} \); this corresponds to a loss of \( 1/e \) in intensity over a length of \( 10^4 \) \( \mu \)m. Since this is much larger than the characteristic
length scale at which the defects in this study are designed at, it can be neglected for the most part, except for situations where absorptive losses are relevant, such as in the calculation of losses along a waveguide.
Chapter 3
Point Defects

In this chapter, I will explore some of the properties of resonant electromagnetic modes trapped at point defects in inverse opal photonic crystals. The defects under study are of two types, both substitutional defects. The first type is the replacement of an air sphere in the inverse opal lattice with a smaller sphere. The second type is the filling of an air sphere with a dielectric material, thereby changing its refractive index. For the remainder of this thesis, I will refer to these as type I and type II defects, respectively.

Figure 3.1 – Point defect structure under consideration. An exploded view of a defect (red sphere) in a lattice of air spheres embedded in a background refractive index of 3.9. The horizontal planes in the picture are the (111) planes of the crystal. Type I defects are formed by making the radius of the defect smaller than the bulk; type II defects are formed by filling it with a higher-index dielectric.

3.1 – Type I Point Defects

The first defect type under study, type I, consists of a substitution of an air sphere with nominal radius \( r_0 \) by a smaller sphere with radius \( r < r_0 \). The colloidal dispersions used to grow opals consist of spheres with a roughly Gaussian distribution of sizes. While the standard deviation is typically very small due to the homogeneous growth process, there inevitably exist
a number of colloidal particles that lie far out on the tails of the distribution, and these can contribute to intrinsic defects of this nature. The calculations undertaken in this section thus apply not only to engineered defects, but also to the intrinsic defects encountered regularly in self-assembled photonic crystals.

Spheres with radii greater than \( r_0 \) are also present intrinsically; however, their incorporation into the crystal lattice during the growth process must necessarily lead to dislocations in the crystal lattice\(^{36}\). These dislocations disrupt the crystal’s symmetry far from the location of the defect itself, propagating along the opal’s growth direction for many hundreds of periods. As such, the oversize spheres cannot be physically incorporated into the lattice and remain a \textit{point} defect. Therefore, in this chapter I will consider only \textit{undersized} spheres and their associated photonic states.

3.1.1 – PWE Studies of Type I Point Defects

The plane-wave expansion may be employed to study point defects by the use of the supercell technique\(^{37}\). In this approach, the “unit cell” employed in the calculation is actually a single unit cell duplicated over an integer multiple of each lattice vector. The result is an \( m \times n \times l \) block of unit cells, called a supercell. The band structure of a defect-free \( 3 \times 3 \times 3 \) supercell is shown in Figure 3.2b. The density of photonic states is constant, but the supercell represents a volume that is larger than the primitive unit cell by a factor of 27; therefore, to find solutions at frequencies equal to that of the 8\(^{th}\) band of the primitive unit cell, 216 bands must be calculated. This large number of bands is apparent in the graph; they are the result of “folding in” states with \( k \) vectors that lie outside the first Brillouin zone. The most notable feature is the complete band gap which is now clearly visible between \( \varphi_b = 0.712 \) and \( \varphi_t = 0.771 \).
3.1.2 – Calculation of Defect States

The supercell may be modified to include a type I point defect by changing the radius of one of the spheres at the center of the $3 \times 3 \times 3$ supercell. In doing so, we expect to find defect states inside the band gap. To perform this calculation, 256 bands were calculated to include states above the gap, as this is a dielectric (donor-like) defect which pushes states down into the gap from above. The grid spacing was $12 \times 12 \times 12$ points per unit cell, or $48 \times 48 \times 48$ for the entire supercell. The calculation took about five hours for each of the 26 points in reciprocal space.

3.1.3 – Band Structure of a Particular Defect

The results of a typical type 1 defect band structure calculation are shown in Figure 3.3, which is zoomed in on the complete PBG region for clarity. This particular result is for $r = 0.9r_0$. Band 217 has been pushed down into the gap. (The significance of the numbering of the bands is spurious; if a larger supercell had been used, this state would have a larger number associated with it, as more bands would have been folded in to the first Brillouin zone at lower frequencies. 217 is simply the lowest band above the complete PBG for this particular supercell: 8 bands below the gap, times $3^3 = 216$.)
Figure 3.3 – Band structure of a $3 \times 3 \times 3$ supercell with a type 1 defect of $r = 0.9r_0$, showing the defect state associated with Band 217, the blue line at $\varphi = 0.72$. Some higher defect bands have also been pushed down into the gap.

In contrast to the extended photonic states associated with the bulk crystal, which vary considerably in frequency across the band structure, the defect state is a flat band – the frequency is independent of direction in reciprocal space. In other words, there is no intrinsic directionality associated with this state – it is a truly localized defect. Another interpretation for this is that the group velocity of the wave, $d\omega / dk$, is very small (essentially zero), which is what one would expect for a localized or “trapped” photon. The spatial distribution of the electric field power is plotted along with the dielectric function in Figure 3.4. The shape of the mode is a six-lobed torus, lying in the (111) plane of symmetry. The field distribution will be important in the study of the coupling between individual point defects.
3.1.4 – Variation of Defect State Frequencies vs. Defect Radius

The radius of the defect may be varied systematically from $r = r_0$ to $r = 0$; the behavior of the bands in the neighborhood of the complete band gap, as a function of the defect radius, is shown in Figure 3.5. The dotted lines represent the maximal (bottom) and minimal (top) extent of the bulk inverse opal band structure; as such, these define the range of frequencies which may be considered within the complete band gap.

It should be apparent from the plot that the bands are pushed down in 3 clear groups. The first group consists of only Band 217 and is very well-defined. The next six bands (218 through 223) come down in a secondary group, tightly clustered. Finally, a third group of higher bands is pushed down into the gap.
Figure 3.5 – Variation in type I defects, calculated by the plane-wave expansion. The value at each point represents the average across all of the 13 points in reciprocal space used in the calculation. The error bars represent the range of those values; small error bars thus identify localized states with flat bands. Outside the limits of the PBG (dotted lines), the photons are unconfined and behave like regular extended states, with non-zero group velocity.

3.1.5 – FDTD Studies of Type I Point Defects

Isolated point defects can be studied by the FDTD method by constructing a simulation region with the defect located at the center and exciting the defect with a short pulse from a radiation source, and observing the field in the cavity after the pulse has ended. Since defect modes are localized and non-propagating, one can observe the cavity ringing down after the excitation. In this study, the duration of the excitation pulse was 250 fs and the duration of the simulation was 2000 fs. The electric field at the center of the cavity is monitored; a plot of the field magnitude vs. time is shown in Figure 3.6b.
Figure 3.6 – Top left: Refractive index in a slice through the center of the FDTD simulation region. The boundaries are the perfectly matched layer. Top right: The electric field magnitude at the cavity center shows the excitation pulse and cavity ringdown. Bottom left: the axisymmetric radiation pattern of an electric dipole\textsuperscript{38}. Bottom right: the cavity dipole excitation spectrum. Note that the complete PBG upper and lower limits are 200.5 and 186.2 THz.

A slice through the cubic simulation region is shown in Figure 3.6a. The walls are an absorbing boundary (perfectly-matched layer)\textsuperscript{39} which is meant to simulate waves propagating freely away, without any back reflections. As such, the simulation region represents a small crystal of finite size. The tight confinement of resonant modes and evanescent nature of the tails that extend away from the defect mean that losses due to the boundary layer are small, even though the boundaries are only a few lattice periods away. The spatial resolution of the simulation was chosen to be 26.45 nm, or 30 cells per sphere diameter.
A dipole-like radiation source was placed at the center of the cavity with the dipole axis aligned along one of the directions in the \{111\} family. The axisymmetric dipole radiation pattern is shown in figure 3.6c. Since dipoles radiate in all directions except along the axis, the dipole excites all of the modes on the edge of the Brillouin zone. This radiation source therefore can excite a cavity mode independent of its orientation; all directions in reciprocal space can thus be studied simultaneously. The frequency content of the excitation pulse was such that it spanned the complete PBG, therefore exciting any defect states that may be present. The spectrum of the excitation pulse is shown in Figure 3.6d.

3.1.6 – Cavity Ringdown Spectrum

A plot of the electric field vs. time for the type I defect with \( r = 0.9r_0 \) – the same defect as in Figure 3.3 – is shown in Figure 3.7. The plot has been truncated to exclude the first 250 fs of data, which is the extent of the excitation pulse. This is to focus on the ringing modes left in the cavity after the excitation has passed.

![Electric field in a type I point defect cavity](image)

Figure 3.7 – Electric field in a type I point defect cavity, with the first 250 fs (corresponding to the excitation pulse) cropped out, plotted on a logarithmic scale. Fitting the plot to a line allows the time constant of the exponential decay to be extracted. The field decays by a factor of e in 450 fs.
If this field is plotted with the vertical axis on a logarithmic scale, a line may be fit to the envelope of the oscillation; the slope of this line is the time constant $\tau$ in the equation for an exponential decay:

\[ E(t) = E_0 \cos(\omega_0 t) e^{-t/\tau} \]  

(3.1)

This time constant $\tau$ is called the photon lifetime; it is the time it takes for the damped oscillation to decay by a factor of $e$. For this particular defect ($r = 0.9r_0$), the photon lifetime is 450 fs. The photon lifetime is related to the quality factor ($Q$) of the cavity by the simple equation:

\[ Q = \omega_0 \tau \]  

(3.2)

where $\omega_0$ is the center frequency of the oscillation. The value of this frequency is just the frequency associated with the single defect band shown in Figure 3.3. In real (non-normalized) units, this frequency is 192.2 THz; therefore the quality factor for this particular defect is approximately 86.5. As resonant cavities go, this is a relatively low quality factor, indicating substantial losses.

3.1.7 – Spectral Analysis of Cavity Ringdown

The decaying field envelope measurement of the previous section does not provide much insight into the trapped states at the defect site, and in fact breaks down entirely if there is more than one state present. A more useful approach is to move to the frequency domain and analyze the spectral content of the electric field signal. This can be done by taking the cropped electric field signal from Figure 3.7a, and performing a fast Fourier transform. The spectrum of the $r = 0.9r_0$ defect is shown in Figure 3.8.
The spectrum is sharply peaked about the frequency 197.5 THz; the lineshape is that of a damped harmonic oscillator. This lineshape is known as a Lorentzian, which is described by the equation

\[ f(\omega) = \frac{A}{2\pi} \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2} \]  

(3.3)

where A is the peak amplitude, \( \omega_0 \) is the center frequency, and 2\( \gamma \) is the FWHM of the peak. The fit of the cavity spectrum to the Lorentzian is shown by the red curve in Figure 3.8. The width of the peak (2\( \gamma \)) describes the damping in the system and is the reciprocal of the photon lifetime \( \tau \); the quality factor Q is then related to the peak’s width by
\[ Q = \omega_0 \tau = \frac{\omega_0}{2\gamma} \] (3.4)

By fitting the spectrum of the point defect cavity to a Lorentzian, the defect mode frequency \( \omega_0 \) and the quality factor can be extracted.

3.1.8 – Center Frequency vs. Defect Radius

The center frequencies and quality factors of each peak are plotted against the radius of the defect sphere in Figure 3.9. The fact that this technique relies on spectral analysis of resonant modes means that states outside the band gap do not show up in the spectrum; therefore, only states within the gap show up on this plot. The black curve in Figure 3.9a can be identified as band 217 from Figures 3.3 and 3.5. Similarly, the red curve can be identified as the family of five closely-spaced states above that. Since the frequencies are so closely spaced, and the simulation time is limited to a few picoseconds by the constraint of a reasonably-short computation time, the individual peaks cannot be resolved. Finally, a third peak is pushed down into the gap as the size of the defect sphere approaches zero.

The quality factor of the cavity tends to increase as the defect radius is decreased, indicating stronger confinement of the trapped states. The maximum \( Q = 212 \), for a defect sphere radius of 125 nm. Note that the flatness of both sets of curves at the final few points is an artifact of the limited size resolution of the grid spacing – the defect sphere was small enough to fit inside a single grid point, and therefore the effective geometry of the simulation was unchanged over the last few simulations.
3.2 – Studies of Type II Point Defects

Type II defects are those defects where the air (refractive index ≈ 1.003) sphere has been filled by a higher-index material. For the purposes of this thesis, I have focused on type II defects with an index between 1 and 2, as this range encompasses a large variety of dielectric materials including numerous polymers and glasses. These defects are more amenable to manufacture than higher-index structures and provide a more plausible structure to study. These defects may be studied in essentially the same way as type I defects; the structure specification is simply modified in refractive index rather than in the size of the defect sphere. For the sake of brevity, I will omit the details of how the calculations were performed, as it is essentially the same as in Section 3.1, and instead simply present the results.

3.2.1 – Bands calculated via the plane-wave expansion

Figure 3.10 shows the variation of the 10 bands above the gap with the refractive index of the defect sphere. In this case, a family of three bands is pushed down first, with a larger number hovering above the gap.
Figure 3.10 – PWE calculated bands vs. refractive index of a type II defect, averaged in the same way as in Figure 3.5. The three highest bands above the gap are pushed down through the band gap as a group.

3.2.2 – FDTD Calculated Resonant Spectra

FDTD was used to carry out a similar calculation for the type II defects as for the type I defects. In the case of the type II defects, only one peak was observed to move across the complete PBG. The PWE calculations indicate this is actually a triplet of states, though the spectrum in Figure 3.11 only shows a single peak. Again, this is due to the limited resolution of the Fourier transform due to the short run time of the calculation. Nevertheless, fitting the resonance peak to a Lorentzian, we can extract a center frequency $\omega_0$ and quality factor Q for this family of states. The variation of these parameters with the refractive index of the defect is shown in Figure 3.12. A clear monotonic trend is seen, with the center frequency decreasing as the defect index is increased. The quality factor increases with the refractive index, reaching a maximum at $Q = 247$ for $n = 1.85$. 
Figure 3.11 – Resonant mode spectrum of a type II defect with defect refractive index 1.5 (left). The squares are the calculated spectrum and the red line is the Lorentzian fit.

Figure 3.12 – Variation of $\omega_0$ and $Q$ vs. $n$ for an isolated type II defect, with dotted lines representing the extent of the photonic band gap (right). The frequency decreases with index, while the quality factor tends to increase, reaching a maximum at $Q = 247$. 
3.3 – Discussion of Results

In this section I will discuss the results of the previous sections on type I and II defects, and compare the results of the PWE and FDTD calculations to each other. I will point out trends and similarities between the two defect classes and some of the limitations of each technique. Finally, the application of these results to the construction of waveguides and other embedded devices in photonic crystals will be considered.

3.3.1 – Comparison between FDTD and PWE results

The plots of type I and type II defect frequencies are reproduced for the sake of comparison in Figures 3.13a and 3.13b, respectively. Each plot shows the results of the FDTD spectra fitting in solid lines and the PWE band calculations in dotted lines. The agreement between the type I FDTD and PWE numbers is poor. Band 217 (black lines) is qualitatively similar, but the higher resonant bands (red and blue lines) have a very poor agreement.

On the other hand, the type II defects agree well over the range investigated. The PWE curves are about 3% higher frequency than the FDTD curve at all points. This may be attributed to the low resolution used (only 12 grid points per unit cell, due to the use of the supercell). Referring back to Figure 2.6, it can be seen that the low resolution introduces an error in bands at these frequencies, calculating them about 3% too high. With this in mind, we see that the type II defects agree fairly well across the two techniques.
Type II defects, which are a variation in the refractive index over an entire sphere, have much better numerical agreement between these techniques than the type I defects, which are a variation in the size of the defect sphere. Since three-dimensional calculations of these kinds require memory that scales cubically with the spatial resolution, the numerical accuracy is often limited by the resolution. The resolution used in these calculations – roughly 10-20 grid cells per sphere diameter – can introduce large errors when the curvature of the structures are of the order of the spacing between cells. Band 217, for example, is pushed entirely through the PBG by a change in the sphere size of a few grid points. In other words, the defect states are highly sensitive to the size of the spheres, and this introduces a great deal of numerical inaccuracy. On the other hand, the type II defects change the refractive index over a large number of grid cells, and therefore any error is more distributed.

3.3.2 – Comparison of Type I and Type II Defects

At first blush, the behavior of the two defect types seems fairly different. However, consider a type I defect, where the radius $r$ is less than the radius $r_0$ of the lattice spheres, by a factor of $\alpha$:

$$r = \alpha r_0$$  \hspace{1cm} (3.5)
One may assign an *effective* refractive index to this defect sphere by averaging the refractive index over the volume of the original lattice sphere. By treating the defect as a spherical core-shell structure with outer radius $r_0$ and inner radius $r$, the expression for the effective refractive index is

$$n_{\text{eff}} = \alpha^3 n_{\text{core}} + (1 - \alpha^3) n_{\text{shell}}$$

where for this work, $n_{\text{core}} = 1$ and $n_{\text{shell}} = 3.9$.

The effective index for the type II defects is simply the refractive index of the sphere-filling material used in the calculation. Figure 3.14 is a plot of the bands calculated by the PWE method vs. the effective index. The first defect state to be pushed down into the gap, Band 217, agrees across these calculations; however, the higher-order bands do not match. This may be caused by the spatial distribution of the field profiles associated with the individual modes; the higher-order defect states have a more complex geometry than the simple shell shown in 3.4, and perhaps the notion of the effective refractive index breaks down when the symmetry of the mode profile does not match the symmetry of the defect itself.
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Figure 3.14 – Plots of the six bands above the gap for type I (solid line) and type II (dotted line) defects. By assigning an effective refractive index to the type I defects, the first-order defect states (type I – black; type II – blue) agree, while the higher-order defect bands (red and green) do not.

3.4 – Applications: Optical Resonators and Gain Media

One particularly useful application of an isolated point defect embedded within a photonic crystal is as an optical microcavity. Much of the work in this chapter has been on the study of photonic states confined to a point defect, with a particular application in mind – that of an embedded microlaser. A laser has three essential components: an optical cavity, a gain medium, and an energy source (pump). A trapped photonic state (or cavity mode, to use the laser language) at a defect that contains a gain medium of some kind can act as a microlaser if the optical gain is greater than the losses. Some potential gain media are shown in Table 3.1, and illustrations of each type are shown in Figure 3.14.
<table>
<thead>
<tr>
<th>Gain medium</th>
<th>Laser Type</th>
<th>Emission Mechanism</th>
<th>Pumping Mechanism</th>
<th>Emission λ</th>
<th>Defect Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$^{3+}$ doped SiO$_2$</td>
<td>Solid state</td>
<td>Fluorescence</td>
<td>Optical</td>
<td>1.54 µm</td>
<td>Type II</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(980/1480 nm)</td>
<td></td>
</tr>
<tr>
<td>PbS nanocrystals</td>
<td>“Dye”</td>
<td>Fluorescence</td>
<td>Optical (550 nm)</td>
<td>1-1.6 µm</td>
<td>Type II</td>
</tr>
<tr>
<td>Helium/neon gas</td>
<td>Gas</td>
<td>Arc discharge</td>
<td>Electrical</td>
<td>1.52 µm</td>
<td>Type I</td>
</tr>
<tr>
<td>Semiconductor p-n junction</td>
<td>Diode</td>
<td>Radiative $e^+/h^+$ recombination</td>
<td>Electrical</td>
<td>??</td>
<td>Type I/II</td>
</tr>
</tbody>
</table>

Table 3.1 – Potential lasing systems for the point defects considered in this thesis.

3.4.1 – Er-doped silica (type II)

Silica doped with rare-earth metals (notably erbium) is a well-known and well-studied gain medium, often used in fiber loop lasers. The C-band has strong gain around the 1.55 µm (192.9 THz) telecom wavelength and can be pumped by light at 980 and 1480 nm. A type II defect with a refractive index of about 1.5 would have a cavity mode at this frequency. Colloidal SiO$_2$ microspheres have been doped with Er$^{3+}$ by ion implantation; using these spheres as a type II inclusion defect would create a resonant cavity with gain at the proper frequency.

3.4.2 – nc-PbS quantum dot (type II)

Dye lasers use a fluorescent molecule as the gain medium; a well-known example is Rhodamine 6G, which has a broad emission peak in the green portion of the optical spectrum. The active molecule is generally dissolved in an organic solvent and pumped through an optical cavity, for cooling and to continuously refresh the supply of molecules in order to prevent photobleaching of the dye. An inverse opal containing a type I defect and infiltrated with a dye could function as a microcavity laser; but the refractive index of the solvent will shrink the band gap unacceptably.

An alternative is to localize the dye just at the defect, by inclusion of the dye in a polymer that is used to make a type II defect. However, as the few dye molecules present at the defect are never replaced, the useful lifetime of the laser will be very short due to bleaching. Instead of a
dye, I suggest nanocrystalline quantum dots, which can be incorporated into polymers, have size-tunable emission spectra, and are far more stable to bleaching over macroscopic time scales. A suitable material is lead sulfide; PbS nanocrystals have a fluorescence peak in the near infrared that is size-tunable up to the desired 1.5 µm wavelength. A cluster of such quantum dots embedded in a polymer-based type II defect could thus behave like a dye-based microlaser.

3.4.3 – HeNe gas (type I)

The systems considered above rely on optical pumping by light at short wavelengths. Electrical pumping is another option; gas and diode lasers rely on collisions from hot electrons to create a population inversion in the gain medium. A gas medium is an attractive one for the high refractive-index contrast it allows. The helium-neon (HeNe) laser, well-known for its red light emission at 633 nm, also has emission lines in the infrared, including one at 1.52 µm. The HeNe works by electrical discharge through the gas mixture; by placing an inverse opal with a type I defect in a HeNe atmosphere and discharging an electrical current through it, photons may be generated. It remains to be seen whether such a discharge would damage the inverse opal or if, through suitable engineering, a non-destructive technique could be found.

3.4.4 – Semiconductor p-n junction (type I/II)

Finally, the semiconducting nature of the silicon inverse opal leads one naturally to consider a diode microcavity laser where the lattice itself is divided into p- and n- type areas, and a p-n junction is formed at the location of a type I or II defect. Silicon is a poor candidate material as it is an indirect bandgap semiconductor and is thus only weakly luminescent. Compound semiconductors with a direct bandgap emit strongly; a particularly strong candidate is gallium arsenide. GaAs has a refractive index of 3.3 – which is lower than Si but above the threshold of 2.85 for the existence of the photonic band gap – as well as low (0.5 cm⁻¹) intrinsic absorption of above 880nm. By placing a type I or II defect at the p-n junction, light emitted by the diode can be trapped at the defect site.
3.5 – Conclusions

In Section 3.3.2, I showed that the frequency dependence of type I and type II defects are essentially equivalent in light of the effective index of type II defects. Calculations of the properties of type I defects were also seen in Section 3.3.1 to be less accurate than type II, due to the finite size of the grid cells. Furthermore, type I defects are shown in Section 3.1.4 to be highly sensitive to changes in the defect sphere radius. While this strong sensitivity of the defect state frequency to the defect radius can be useful for a tunable microcavity – a size-tunable defect would offer a much greater frequency shift than adjusting the refractive index (by e.g. electro-optic or chemical means) – it is a bad thing when one is interested in guiding light along defects, around corners and so on.

Therefore, for the rest of this thesis, which focuses on the coupling between defects for the purposes of wave guiding, I will focus on type II defects: higher-index inclusions. This type of defect are more accurate to simulate, easier to fabricate, and less sensitive to unintended variations in the geometry. With that in mind, I will turn now to the study of coupled point defects.
Chapter 4

Waveguides

The main thrust of this thesis is the design of embedded linear defects suitable for guiding light within a photonic crystal. In this chapter, I will discuss a design for a waveguide based on the work in the previous chapter on point defects.

4.1 – Wave guiding with photonic crystals

PC waveguides of many flavors have been the subject of intense study, particularly in the realm of two-dimensional photonic crystals. 2D PC waveguides have a slab geometry, with a periodic modulation of the refractive index within the plane of the slab. In this approach, the photonic band gap of the 2D crystal confines the light to the waveguide in the plane of the crystal slab. The out-of-plane confinement is achieved by total internal reflection, which requires a lower-index cladding layer above and below the waveguide slab. The simple planar geometry allows for the use of established microfabrication tools such as photolithography and standard deposition techniques, enabling precise control over the structure of the photonic crystal and waveguides. This has been a very successful approach, but ultimately this technology is limited by out-of-plane losses. The ideal structure to fully realize the potential of photonic crystals is a waveguide that is entirely enclosed by a complete 3D photonic band gap cladding.

4.1.1 – Top-down 3D photonic crystal waveguides

Three dimensional structures are difficult to fabricate. One successful approach is direct laser writing (DLW), in which an infrared laser beam is focused to a point inside a layer of photoresist. At the waist location, where the intensity is greatest, a nonlinear two-photon absorption process can occur, exposing a small ellipsoidal region at the focus, while leaving the surrounding areas unexposed. By scanning this voxel through the resist layer, an arbitrary 3D shape may be written within the resist layer. This technique has been successfully used to fabricate a waveguide inside a 3D photonic crystal layer. However, the structures that can be fabricated in this manner are limited in size due to mechanical stresses in the resist layer that occur during the exposure process.
4.1.2 – Top-down waveguides in bottom-up templates

A promising alternative is to use a self-assembled opal template as a bulk 3D material, and to inscribe a linear defect within the structure using a top-down method such as photolithography or DLW. This combines the advantages of the self-assembled photonic crystal (high regularity, large area, low cost) with the precision and flexibility of an externally written defect. Both of these techniques (DLW\textsuperscript{49} and photolithography\textsuperscript{50}) have been employed to write rectangular or cylindrical channels within an opal photonic crystal. However, both of these structures are considerably larger than the lattice constant of the opal in which they are written, which complicates the task of understanding and controlling their wave guiding properties.

In this chapter, I will study the guiding of light along linear defects in an inverse opal. In the previous chapter we saw that point defects, such as a filled air cavity in an inverse opal, can trap light and resonate at well-understood frequencies. Since the evanescent electromagnetic field of the trapped light extends away from the site of the point defect, light can couple into another defect placed nearby. This notion of a chain of coupled oscillators is similar in concept to the coupled-resonator optical waveguides\textsuperscript{51} (CROWs) that have been studied previously, but on a much more compact scale.

4.2 – The inverse opal coupled-defect waveguide

In Chapter 3 we explored both type I (substitution of a lattice air sphere with a smaller radius) and type II defects (substitution of a lattice air sphere with a higher index) and saw that the resonant frequencies are essentially equivalent. In this chapter I will focus on the study of waveguides made up of type II defects. Therefore the waveguide under study will be made up of an inverse opal, with selected air spheres filled by a higher-index material. This has the advantages of better numerical accuracy in these calculations, ease of fabrication, and the potential to incorporate active materials into the structure of the waveguide.

4.2.1 – Waveguide parameters

Even with these constraints, a number of choices remain in the design of a waveguide. The first is the question of which spheres should be filled and what their spatial relationships should be. Intuition compels the hypothesis that a good waveguide should lie along one of the high-
symmetry directions of the photonic crystal template. The thin film self-assembly process generally results in opals oriented with the (111) crystal plane oriented parallel to the substrate.

The Γ-K or [110] direction is especially attractive, as it is the direction of close packing and therefore coupling from adjacent defects should be strongest. By the symmetry of the FCC structure, there are actually 12 equivalent directions within this family. Six of these directions lie in the (111) plane, which is reflected in the hexagonal packing of the opal layers. If we treat the opal as an infinite crystal for the purposes of our calculations, any of these directions is equally viable. Therefore, the results apply to any waveguide oriented along one of the principal [110] axes. Furthermore, we should expect that sharp bends should be through an angle of 60°, rather than the oft-quoted 90°, as it reflects the structure of the lattice. The coupled-defect waveguide in question is made by simply filling a row of air spheres along one of the [110] directions with a high-index material. This row of spheres is embedded below the surface of the photonic crystal, such that the waveguide is enclosed on all sides by the inverse opal structure. It is to the study of these waveguides that we now turn.

4.3 – PWE waveguide calculations

In describing the [110] coupled-defect waveguide, I have deliberately not specified the refractive index of the material used to fill the air spheres, in order to leave this as a free parameter. In Chapter 3 we found that an isolated type II point defect supports a single resonant mode over the range of \( n_{\text{defect}} \approx 1.3 - 1.7 \). It should be expected, then, that a waveguide made of coupled defects of this type will propagate a wave over roughly the same range of refractive indices.

4.3.1 – Frequencies of guided modes

Dispersion diagrams (frequency vs. wave vector \( k \)) of defect states associated with such a propagating wave can be calculated using the plane-wave expansion method. The supercell technique can be employed again, this time using a modified slab-like supercell which is shown in Figure 4.1. In this case, a \( 3 \times 3 \times 1 \) supercell of the standard primitive unit cell was used, with the defect sphere located at the center. By specifying that the PWE calculation use only those values of \( k \) which lay along the direction of propagation – perpendicular to the face of the slab – the frequencies calculated are those associated with defect states that propagate along the waveguide axis.
Figure 4.1 – Plot of the refractive index distribution used in the PWE supercell calculation. To show the linear nature of the defect, the slab has been replicated over three periods along the waveguide axis. A volume plot of the three dimensional supercell is shown (left), with the [110] face visible at the front. Waves propagate down this axis along the defect spheres, which are embedded inside the volume. A horizontal slice through the data set (right) shows the defect spheres \( n = 1.55 \) in light blue, surrounded by a cladding of dark blue air spheres \( n = 1 \).

A plot of several example dispersion relations is shown in Figure 4.2, showing that a triplet of states has been introduced into the complete band gap. For this calculation, a resolution of 24 grid points per unit cell was used, and the size of the supercell dictates that 72 bands \( (3 \times 3 \times 1 \times 8) \) are required to reach the complete band gap between the 8th and 9th bands.

Taking the three states together and treating the structure as a multimode waveguide, we may estimate the transmission properties of the waveguide using the local density of states approach. The basic idea is to generate a histogram of the frequencies associated with this triplet of states, which can be interpreted as a crude transmission spectrum. Fitting this spectrum to a Gaussian, we can extract the center frequency and a bandwidth, which I define as the FWHM of the fitted curve. An example histogram is shown in Figure 4.3, along with a plot of how the bandwidth and center frequency varies with the refractive index. We see that for the range of defect index from approximately 1.45 to 1.8, the center frequency lies entirely within the complete PBG. Light of \( \lambda = 1.55 \, \mu m \) will be guided if the refractive index of the defect spheres is between 1.5 and 1.72.
Figure 4.2 – Examples of dispersion relations (ω vs. |k|) calculated by the plane-wave expansion method, for defect spheres of index n = 1.55 (left) and n = 1.75 (right). The vertical axis is frequency, with dotted lines indicating the limits of the complete PBG, and the horizontal axis spans the first Brillouin zone along the Γ-K direction. The gray areas at the top and bottom are those regions filled by the propagating modes of the bulk crystal. As the index is increased, three states (bands 73, 74 and 75) are pulled down into the band gap.

Figure 4.3 – The local density of guided states for the n = 1.75 waveguide (left). The green bars are a histogram of the frequencies in Figure 4.2b, and the red line is a Gaussian fit. Repeating this process and varying the refractive index yields a plot of the bandwidth and center frequency of our coupled-defect waveguide (right). The shaded red region represents the full wavelength extent of the propagating modes. Choosing n = 1.65 places the center frequency of the waveguide at 1.55 µm.

As with the point defects studied in Chapter 3, increasing the defect index further causes these first-order modes to be pushed further down until they are below the PBG. Accordingly, higher-order modes are also pulled down into the gap. These higher-order modes may also be used for
guiding light, but for the time being I will, for the sake of simplicity, focus on the study of the lowest-order defect states (bands 73-75).

4.3.2 – Field distributions

The plane wave expansion technique outputs both the eigenvalues and the associated eigenvectors that are solutions to the modified wave equation (Equation 2.7). The former can be identified as the frequencies that are plotted in the band diagrams above, and the latter as the spatial distribution of the electromagnetic field associated with each band. As such, we can plot the fields to verify that the photonic state is indeed a defect state. Figure 4.4 shows plots of the electric field intensity for two bands – Band 72, which I have identified as a non-localized state associated with the bulk crystal, and Band 73, which I have identified as a localized state associated with the defect. We see that the bulk state is distributed throughout the crystal, while the bound state (band 73) is highly confined to the waveguide structure. Since most of the electric field power is located in the defect spheres, we can conclude that this is indeed a bona fide guided wave. The other two states in the triplet identified in Figure 4.2 have similar field distributions.

4.4 – FDTD calculations

The plane-wave expansion approach gives us considerable insight into the frequency-domain behavior of the waveguide and the photonic states which it can guide. However, a wave propagating down a waveguide is an inherently time-domain sort of problem, so we can expect time-domain tools to be especially useful here. In this section, I will discuss the results of FDTD modeling of the coupled-defect waveguide above.
Figure 4.4 – Time-averaged electric field ($|E|^2$) distribution as calculated by the PWE technique, for a non-localized bulk state below the photonic band gap (band 72, left) and a guided defect state (band 73, right). The plot shows the magnitude of the electric field in a (111) plane located at the center of the waveguide spheres. The refractive index profile associated with this view is the same as that shown in Figure 4.1b.

4.4.1 – Simulation parameters

The ideal FDTD simulation would model the entire photonic crystal and waveguide structure, including both the substrate, bulk crystal layers, waveguide and the air above. However, the resolution of the grid used in the simulation must be fine enough to accurately represent the structure down to the level of the individual spheres. Therefore, the constraints imposed by limited computer memory and processing time force some simplifying assumptions to be made when modeling the waveguide using this technique. One such simplification is to model only the portion of the photonic crystal immediately surrounding the waveguide. We are mainly interested in the wave guiding properties of the structure, and therefore with fields associated with defect states which are confined to the immediate neighborhood of the waveguide, as shown in Figure 4.6b. The fields in question have evanescent tails which do extend away from the waveguide structure, but the tight confinement and exponentially decaying magnitude of these fields means that they are almost negligibly small by the time you are a few periods of the crystal away from the waveguide.
The FDTD simulation region is shown with boundaries in orange. The air spheres of the bulk crystal are gray, and the defect spheres are light blue. View down the waveguide axis along the $[110]$ direction (left) and from above along the $[111]$ direction (right). The yellow square shows the region over which the field was measured to determine the output of the waveguide. This particular waveguide is only six spheres (4.7 $\mu$m) long.

Therefore, I claim that the structure may be reasonably modeled with a simulation region that encloses the waveguide in a box-like shape, provided the boundaries of the box are reasonably far away from the waveguide. An example simulation region is shown in Figure 4.5. The boundaries of this region were chosen to be absorbing PML boundaries, which allows any light that lies outside the band gap to be scattered away.

Light was injected from a broadband Gaussian source at one end of the waveguide and the simulation was allowed to run for 1.5 to 4 picoseconds. The field was sampled in the plane of the waveguide as well as at the output. For numerical stability, the computational cell size must be an integer fraction of the periodicity of the structure, so a grid spacing of $r_{sphere}/10 = 39.7$ nm was used. The simulation was repeated multiple times, varying the refractive index of the defect spheres.

4.4.2 – Waveguide transmission spectra

By integrating over the output window shown in Figure 4.5, the transmission spectrum of the waveguide may be calculated. Spectra for waveguides of various refractive indexes are shown in Figure 4.6. As the index is increased to about 1.65, a group of transmission peaks is pushed
down from above the band gap, as was seen with the PWE method. Further increasing the refractive index introduces other additional peaks in the transmission spectrum, corresponding to the higher-order defect states discussed in Section 4.3.1.

Figure 4.6 – FDTD calculated transmission spectra for a range of waveguide refractive indexes. Dashed vertical lines represent the upper and lower extent of the photonic band gap. The vertical axis has been offset for clarity.

The multiplicity of peaks in the transmission spectrum is due to a Fabry-Perot resonance of the waves transmitted through the waveguide. This is an artifact of the simulation region’s finite length and is due to an impedance mismatch at the absorbing boundaries at the ends of the simulation region. This can be verified by varying the length of the simulation region, as shown in Figure 4.7. Note that for improved spectral resolution, the simulation time was increased by a factor of five as compared to Figure 4.6. This has the effect of sharpening the resonance peaks. As the length is increased from 5 to 15 sphere diameters, the resonance shifts, and the spacing and intensity of the Fabry-Perot peaks is seen to decrease. In the limit of infinite length, a smooth transmission spectrum should be seen.
Figure 4.7 – Transmission spectrum of the n = 1.55 waveguide, for various lengths of the simulation region. As the length is increased, the Fabry-Perot peaks become closer together and less pronounced. Here the length is given in units of the sphere diameter.

With this notion and the shape of the blue curve in Figure 4.7 in mind, we may analyze the bandwidth of the waveguide by fitting the spectra of Figure 4.6 to a single Gaussian and extracting the FWHM of each peak. The results of the fitting are shown in Figure 4.8. The behavior of the waveguide as a function of the refractive index is qualitatively the same as that calculated by the PWE method. The FDTD-calculated bandwidth is slightly lower, but the essential features are the same.
Figure 4.8 – Plot of the center frequency (red) and bandwidth (blue) of the $n = 1.55$ waveguide. Choosing the index to place the center of the transmission peak at $1.55 \, \mu$m yields $n = 1.62$, close to the value in Figure 4.4.

4.4.3 – Field distributions

By sampling the electromagnetic fields in the simulation at each time step, one can generate plots of the spatial field distribution. Figure 4.9 is a plot of the electric field magnitude, represented by the color axis, which has been zoomed in so that the faint fringe fields that extend perpendicular to the waveguide are visible. The location of the source is indicated by the yellow $X$. It is clear that the electric field is strongly confined to the waveguide, and that each sphere in the chained-sphere waveguide supports a point-defect-like state. The field profile is qualitatively similar to the plot in Figure 4.4b of the eigenvector of the 73rd band, indicating that this is indeed one of the defect states seen previously.
The source location is on the left side of the simulation, marked by an x. The variations in the electric field around the edge spheres can be attributed to the proximity of the PML boundary, as can the slight fluctuations in the intensity at individual spheres. The latter is a visible artifact of the Fabry-Perot resonance discussed in Section 4.4.2.

4.4.4 – Wave propagation and group velocity

The main benefit of using a time-domain simulation is that the dynamics of the wave propagation can be studied. Of particular interest is the velocity at which the waves travel down the waveguide; the group velocity, \( \frac{\partial \omega}{\partial k} \), gives the rate at which energy is transferred along the waveguide axis. Figure 4.10 is a plot of the electric field as a function of time, for two points along the \( n = 1.55 \) waveguide: at the source, and at the output window. In this simulation the points are located 15 sphere diameters, or approximately 12 \( \mu \)m apart. By choosing the maximum of the electric field at the rising edge of the pulse as a fiduciary marker, the propagation delay can be measured. In this case it is 550 fs, which corresponds to a group velocity of 0.072c.

This number places the waveguide solidly in the realm of the “slow light” waveguide\textsuperscript{53}, in which the group velocity is much less than it would be in a bulk \( n = 1.55 \) medium or in a planar waveguide circuit. The low velocity can be attributed to the coupled resonator nature of this waveguide – since the structure is made up of point defects in close proximity to one another, light is transferred by coupling through the evanescent tails of the defect states studied in
Chapter 3. The low propagation velocity enables a host of useful applications for waveguides of this kind, as the interaction between the guided light and the waveguide medium are dramatically enhanced.

Figure 4.10 – Electric field vs. time at two points along the coupled defect waveguide, for the n = 1.55 case. The delay in arrival of the rising edge at the output end of the simulation region is 550 femtoseconds.

4.4.5 – Bends and Splitters

Figures 4.4b and 4.9 show that the field distribution is more or less spherical at any given defect along the chain. That this is the case implies that the coupling from one sphere to the next need not be along the same direction; i.e. by the symmetry of the crystal, we ought to be able to couple just as well to any of the 12 spheres that surround a particular defect. Figure 4.11 illustrates this principle nicely, showing how the waveguide mode propagates neatly around 60° bends. This sharp bending is an essential feature of photonic crystal waveguides and provides the basic functionality that an integrated photonic circuit would demand.

The transmission spectrum through this dogleg is plotted in Figure 4.12, along with the transmission spectrum of the normal straight-line waveguide. It is apparent that some losses have occurred during the course of the bending; these can be attributed to reflections at the bend locations. Such reflections are a common feature of sharp bends in 2D PC waveguides, and it
has been found that slight changes to the design of the bend can virtually eliminate these losses. I venture that a similar approach could be taken in this case as well.

Figure 4.11 – Coupled-defect waveguide incorporating two 60° bends, a structure known as a dogleg. The refractive index profile (left) shows the waveguide structure, and the electric field profile clearly follows the waveguide. The source is in the upper left, and the waves travel to the lower right. The fluctuations in the intensity at the various points along the waveguide are again due to the Fabry-Perot resonance caused by the PML boundary layers.

The concept of the waveguide bend may be further extended to a splitter, which allows light from a single waveguide to be divided into two new waveguides. A simple two-way splitter, based on the 60° bend above, is shown in Figure 4.13. By the symmetry of this structure, we expect the power to be split 50/50 down each of the arms. In fact, a good portion of the light is reflected back from the junction, but again, it is my belief that with sufficient engineering, a high-quality splitter can be derived from this basic design.
Figure 4.12 – Transmission spectrum through the dogleg structure. The dashed line is the spectrum of the straight waveguide.

Figure 4.13 – Refractive index profile of a two-way splitter (left). The electric field profile (right) shows the light entering from the left and coupling down both of the splitter’s arms. Some of the light is also back-reflected.
4.5 – Conclusions and Practical Matters

In this and the preceding chapter, I have written somewhat blithely about the placement and nature of defect spheres and how the defect states, transmission spectrum and so on depend on the refractive index. I have done so without specifying what materials these defects might be made of, so that the physics may be allowed to dictate the device design. In this section, I will suggest some candidate materials and propose some other functional devices that might be made by judicious combination of the above circuit elements with appropriate materials.

We have seen in Section 3.3 and in this chapter that type II defects – be they isolated or chained together– support a triplet of defect states when the refractive index of the defect is within the approximate range of 1.45 – 1.85. This is a lucky circumstance, in that an enormous variety of materials and their attendant chemistries fall within this range, making this design highly flexible in terms of material choices. Nearly all organic polymers have a refractive index within this range\(^\text{55}\), as do many inorganic glasses, crystals, and even liquids\(^\text{56}\).

Polymers are an especially attractive candidate class of materials for the defect spheres. They are easily fabricated and formed, mechanically stable, and have a wide range of chemistries. A variety of molecules can be incorporated into the host matrix that can confer a polymeric microsphere with active behavior. A waveguide made of acrylic or polystyrene spheres doped with luminescent dyes or colloidal quantum dots might then act as a channel for signal amplification.

The inclusion of dipolar chromophore molecules\(^\text{57}\) into polymer matrices can confer a high electro-optic coefficient\(^\text{58}\). This property shifts the refractive index of the material upon the application of an external electric field, and has been exploited to great effect in the design of electro-optic modulators. An example modulator based on the waveguide scheme discussed in this chapter is shown in Figure 4.14. The figure shows a Mach-Zehnder interferometer\(^\text{59}\), where light is split into two parallel paths and then later recombined. If the optical path length of the two arms is the same, then at the output the two waves will interfere constructively and the output at the end of the interferometer should be maximized. Conversely, if the path length difference is 180° of phase advance, the two waves will interfere destructively, and the output will be zero. By fabricating one of the arms out of an electro-optic polymer and applying an external electric field, the phase velocity of one arm will change, altering the phase relationship and modulating the output of light from the device. This is a naive and simplistic design, but the essential principle can be employed to design high-quality devices for integration into complex photonic circuits.
In conclusion, we now have a solid understanding of how light propagates down a waveguide comprised of coupled point defects in an inverse opal. We have discovered that the group velocity in such a waveguide is quite small, due to the weak coupling between adjacent defects. Both frequency-domain and time-domain tools can be used to model the behavior of such a waveguide, and the results from each approach have been shown to be in good agreement with each other. Furthermore, we now have a set of basic building blocks – a waveguide, a bend and a splitter – which can be combined and modified to construct devices such as switches, filters, modulators and so on.

One of the useful and important features of this design is that the waveguide incorporates a secondary material into the photonic crystal template. This feature, however, has a downside, in that placing spheres within a self-assembled photonic crystal in precise and predetermined locations is a non-trivial challenge. In the next chapter I will discuss ways these devices might be made, how they stack up to the competition, and which way the future lies.
Chapter 5
Towards the Future

In this chapter, I will review the results found so far, outline an approach to the fabrication of the defect structures I have proposed, compare the results to other technologies, and propose some future directions for research in this area.

5.1 – Review of Results

In Chapter 3, it was found that type I and type II defects both support localized defect states, and that they are essentially equivalent with regard to the frequencies and field distributions of the lowest-order defect states. The frequency of these defect states can be tuned across the entire photonic band gap by varying the effective defect index from 1.4 to 1.9. Treating the point defect as a microcavity, we found that the maximum quality factor was approximately $Q = 250$. In Chapter 4, we saw that the coupling between adjacent spheres can transfer light along a chain of these point defects. The center frequency of the transmission peak can also be tuned across the band gap by changing the effective index of the defect spheres, and choosing $n = 1.65$ enabled us to meet the goal of guiding 1.55 $\mu$m light. The waveguide was found to be multi-mode, with a bandwidth of 30 to 40 nm, and featured a low group velocity of 0.07$c$, making it one of a class of slow light waveguides. Finally, we saw that light could be coupled around tight bends of 60°, enabling the design of compact and functional photonic devices.

5.2 – Approaches to Fabrication

Through the course of this thesis I have written somewhat blithely about the placement of defects, the introduction of novel and functional materials and composite structures made up of precisely placed defects buried in a three-dimensional lattice. However, often the difficult question is not “What should we make?” but “How do we make it?” While the self-assembly of the opal photonic crystals is an inherently bottom-up process, the placement of engineered defects in a photonic crystal is an inherently top-down process. This is a unique challenge – top-down meets bottom-up. What is needed is a fabrication technique that is flexible enough to work with the self-assembled nature of this particular class of photonic crystals.
5.2.1 – Optical techniques

The standard fabrication method for devices and structures at this scale is photolithography. The state of the art in photolithography uses deep ultraviolet light (157 nm) and employs phase-shift masks to sharpen the edges of features as small as 35 nm. This technique has certainly fine enough resolution for the purposes of the photonic crystals considered in this thesis, but the planar nature of the lithographic procedure means that truly 3D structures cannot be made. A more flexible approach is the direct laser write, where multiphoton absorption at the waist of a tightly focused laser forms a small volume of polymerized photoresist. Unlike photolithography, this is a serial process and therefore slower, but defining structures in this way is more flexible, as an arbitrary 3D structure can be written by scanning the focus of the beam through a photoresist.

So, one approach might be to infiltrate an inverse opal with a photoresist polymer, and pattern the polymer with photolithography or with the laser writing scheme. However, these techniques are limited in that they really only make structural modifications to the photonic crystal. The introduction of new materials to the photonic crystal lattice, placed in a desired location, requires a different and more ambitious sort of approach. The defects and structures considered in this thesis have been chosen with a particular fabrication technique in mind that does allow for the introduction of new types of materials, not just structural modifications. This approach is nanorobotic manipulation.

5.2.2 – Nanorobotic Manipulation

Using a robot to manipulate small building blocks in order to build up a composite structure is an extension of what is essentially the most ancient of human construction techniques. The approach has been extended all the way down to the atomic scale, with the use of an STM probe to move individual atoms around on a substrate. Other instruments, notably the AFM, have been employed to manipulate nanometer-scale objects such as carbon nanotubes, nanocrystals, and nanowires. The STM and AFM are scanning probe instruments where the sensing probe has been repurposed as an actuator. Using a sharp scanning probe for imaging allows very small objects to be resolved and therefore moved around.
5.2.3 – Integration with SEM

Unlike nanometer-scale objects, a photonic crystal with a band gap in the optical or infrared has features with dimensions that are order of magnitude equal to the wavelength; generally, a few hundred nanometers or larger. As such, other microscopy techniques can be used for sensing the positions of the objects to be manipulated, and a dedicated actuator can be used to position the objects. This allows for better manipulators, such as microgrippers, tweezers or even multiple actuators acting as nanoscale hands for positioning, as well as simultaneous manipulation and real-time imaging. There are a number of homebrewed and commercial nanomanipulator systems available.

A scanning electron microscope can easily resolve objects with structure on the scale of the inverse opals considered in this thesis. It is this technique – a nanorobotic manipulator coupled with a SEM-based imaging system – which this thesis has been written around. All of the defects modeled so far were designed with fabrication by a nanorobotic manipulator in mind. Figure 5.1 shows an illustration of a commercially available nanomanipulator system, a Zyvex S-100, inside the sample chamber of an SEM. This system, like most, is based on piezoelectric actuation of an end effector, which is used to pick and place sub-micrometer objects. The end effector shown in the figure is a simple probe-like device, but many other end effectors are possible.
Figure 5.1 – Inside the sample chamber of an SEM-based nanorobotic manipulation system (left). A piezoelectric stack actuates a probe, picking up a defect sphere (green) and moving it to an opal (white), where it can be placed into the lattice at any desired position. A sequence of SEM images (right) shows the manipulation process, from picking up a sphere (a-c), transferring it to the opal (d-e), to placing it on the lattice (f).

The proposed approach to the fabrication of engineered defects in an inverse opal is to place the defects in the template opal, prior to inversion. In this scheme, an opal is grown in the ordinary fashion, and placed in the nanomanipulator system. A target sphere is removed from the topmost layer of the crystal, and replaced with a defect sphere. Then, the opal is removed from the SEM chamber and a second layer of spheres is grown atop the first, embedding the defects within the lattice. This pick-and-place process is illustrated in Figure 5.2.
Figure 5.2 – Nanorobotics-based pick-and-place technique for placing point defects in an opal template. A probe is lowered to the surface of an opal (a), and a sphere is removed from the lattice (b). Defect spheres of a different material or size (orange spheres) are introduced (c) and transferred to the probe (d). The defect sphere is placed into the opal lattice (e). This procedure can be repeated to form a larger structure (f). Finally, a second self-assembly step can be used to grow an overlayer of spheres on top of the defect structure, embedding the defects in the 3-d crystal.

5.2.4 – Challenges for SEM-based Nanorobotics

While the nanorobotic manipulation technique is very flexible, it is a serial process and low-speed. It cannot be easily parallelized, though some degree of automation is possible via image recognition and a feedback-based positioning system. Operated in open-loop mode, with probes manually positioned by a human operator, the process of locating a defect sphere, picking it up and placing it in a desired location can take up to an hour.

There are several forces on a target sphere during the manipulation process, but the picking and placing involves a balance of two dominating forces. Electrostatic interactions between electrically charged spheres, which are long-range \((r^{-2})\) repulsive forces, and London-Van der Waals interactions, which are short-range \((r^{-6})\) attractive forces, must be balanced for the manipulation to be successful. Assuming a static end effector, and using the convention that attractive forces are negative, the condition for picking up a sphere from some substrate is

\[
F_{\text{sphere-\text{substrate}}} > F_{\text{sphere-\text{probe}}} \tag{5.1}
\]
while the condition for placing a sphere onto a substrate is

\[ F_{\text{sphere-substrate}} < F_{\text{sphere-probe}} \]  \hspace{1cm} (5.2)

Clearly, there is a need for some degree of tunability in the interactions of the probe-sphere-substrate system. This could be achieved by applying a voltage to the probe, thereby increasing \( F_{\text{sphere-probe}} \) through a reduction of the electrostatic repulsion. However, for microspheres of this size in contact with each other, the adhesion force (stiction) is dominant, and some approach to reducing the stiction is needed.

5.2.5 – Adhesion Forces on a Microsphere

The energy of adhesion between a sphere and a flat substrate is

\[ \Phi = -\frac{A}{12} \left( \frac{1}{x} + \frac{1}{1 + x} + 2 \ln \frac{1}{1 + x} \right) \]  \hspace{1cm} (5.3)

where \( A \) is the effective Hamaker constant, \( x = z / d \), where \( z \) is the spacing between the sphere and substrate, and \( d \) is the diameter of the sphere. Taking the limit where \( z << d \), the interaction energy can be simplified to

\[ \Phi = -\frac{Ad}{12z} \]  \hspace{1cm} (5.4)

The adhesion force on the sphere is then just the derivative of the energy:
The interaction between the sphere and the probe may be treated by modeling the end of the probe as a spherical object with a radius equal to the radius of curvature of the probe tip. A similar derivation for the sphere-sphere force may be carried out, wherein one finds

\[ F_{\text{sphere-substrate}} = \frac{\partial \Phi}{\partial z} = \frac{Ad}{12z^2} \]  

(5.5)

The stiction problem may be illustrated by using the above equations to calculate \( F_{\text{sphere-substrate}} \) and \( F_{\text{sphere-probe}} \). Using an effective Hamaker constant \( A = 2 \times 10^{-20} \) J, microsphere diameter \( d = d_1 = 500 \) nm, probe diameter \( d_2 = 100 \) nm, and a separation of \( z = 5 \) Å, we find \( F_{\text{sphere-substrate}} = 3 \times 10^{-9} \) N and \( F_{\text{sphere-probe}} = 1.5 \times 10^{-10} \) N. The force keeping a particle attached to the substrate is thus a factor of 20 stronger than the adhesion to the probe which is trying to pick it up. This is a simplistic and approximate calculation, but it illustrates the order of magnitude which must be overcome in order to pick up a sphere with a simple probe geometry.

\[ F_{\text{sphere-sphere}} = \frac{Ad_1d_2}{6z^3} \]  

(5.6)

where \( d_1 \) and \( d_2 \) are the diameters of the two spheres.

5.2.6 – Carbon Nanotube Substrates

One way of reducing the stiction is through the use of a non-stick substrate. A carbon nanotube (CNT) forest is a substrate covered with an array of vertically aligned multiwalled nanotubes; microspheres dispersed on the surface of a CNT forest have been experimentally shown to have much lower stiction than a bare substrate \( 71 \), even compared to substrates with low surface energy like Teflon.

A microsphere sitting atop a CNT forest will be in contact with only the ends of a few nanotubes, which have a diameter of only 20 to 30 nm. Calculating the adhesion force between a microsphere and the end of a carbon nanotube by treating the nanotube as a sphere with diameter 25 nm and using Equation 5.6, one finds \( F_{\text{sphere-nanotube}} = 7.5 \times 10^{-12} \) N. Thus, \( F_{\text{sphere-probe}} \approx F_{\text{sphere-substrate}} \) for a sphere in contact with as many as twenty such nanotubes. Figure 5.3
shows a dispersion of microspheres on top of a CNT forest. With the adhesion forces balanced, tuning the electrostatic interactions to enable picking and placing of the microspheres should be possible.

Figure 5.3 – Colloidal microspheres dispersed on a carbon nanotube forest. The low stiction and flexible nature of the surface allows the microspheres to be more easily picked up and moved around by a nanorobotic manipulator.

5.2.7 – Alternative Approaches

Another, more exotic approach might involve the use of a scanning nanopipette probe, loaded with a solution of the desired defect polymer. Recent work with tapered nanopipette tips has achieved attoliter-level control over the volume of liquid droplets. The diameter of such a tip can be as small as 100 nm, allowing it to be inserted directly into the inverse opal lattice, filling a sphere below the surface with the polymer solution. Since the volume of a single air sphere is roughly 250 aL, good control over the size of the polymer droplet injected into the cavity should be achievable. Repeating this process in a stepwise fashion along the crystal could allow one to fill in a line of air spheres with polymeric defects. This process is illustrated in Figure 5.4. Yet another conceivable technique could involve the use of optical trapping to guide defect spheres into their desired positions during the initial self-assembly process.
5.3 – Conclusions and Directions for Future Work

Most of this thesis has been written in the conditional tense, since there remain a number of challenges that must be addressed before the devices I describe can be experimentally realized. First, the assumption in this thesis is one of a perfect single-crystal opal, which requires that intrinsic defects like grain boundaries, stacking faults and so on can be eliminated entirely. Improved control of the microsphere synthesis and self-assembly can address these problems, but a self-assembled system will almost always have some degree of disorder. Further work, then, should be to design structures that are tolerant to defects of this sort. Additionally, the nanorobotic manipulation process outlined above should be improved to enable fast and repeatable movement of the defect spheres. Finally, the coupling of light into this structure from external sources remains a challenge, one that might be met by the use of tapered waveguides, directional couplers and so on, or by the use of photo- or electroluminescence to excite embedded cavities.

Even assuming that all of these goals are met, it seems unlikely that this system will become the platform of choice for the next generation of commercial computer processors. Indeed, there is probably no single answer, any all-optical computer chip will most likely feature a mixture of fiber optics, planar lightwave circuitry, and photonic crystal devices of various geometries. I feel strongly that the direction of future work should be most focused on taking the best of each world and integrating these diverse approaches into a hybridized technology.
This discussion has underscored a fundamental difficulty in nanoscience: namely, that fabrication of three-dimensional structures with complex geometries and multiple materials at sub-micron length scales is not easy. The pick-and-place approach to fabricating defects is an inherently serial process and not really amenable to parallelization for high-throughput manufacturing.

However, there is more to the world than industry. Devices based on the designs in this thesis may never make it to the shelf, but the strong localization of light due to the complete PBG can and has been be exploited for scientific study\textsuperscript{73}, and in this area a low-throughput process like pick-and-place nanomanipulation is acceptable. So often, in the greater field of nanotechnology, basic science has taken a back seat to commercial applications. There remain enormous questions left unanswered in our description of the natural universe, and I feel that this is the area in which this work can contribute most. I look forward to seeing this design, or others like it, continue to advance our understanding of light-matter interactions. Surely that is an admirable endeavor.
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