

Characterisation of Photonic Crystals Fabricated by Holographic Lithography

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Thesis submitted for the degree of

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Abstract

Holographic lithography is a new technique developed for the fabrication of three-dimensional photonic crystals in polymer. Four coherent laser beams are interfered to generate a three-dimensionally periodic interference pattern in a film of photoresist. Subsequent processing steps render a three-dimensional photonic crystal, whose structure is commensurate with the original interference pattern.

Two interference patterns are discussed in detail: a face-centred cubic pattern with a conventional lattice constant of 922 nm in air and a face-centred cubic pattern with a conventional cube side of 397 nm in air (interference wavelength 355 nm). Three types of basis are presented for the interference pattern with a 922 nm lattice constant: a right-handed, a left-handed and a non-chiral basis. Photonic crystals have been fabricated with both a chiral and a non-chiral basis and evaluated by scanning electron microscopy. Optical transmission measurements are presented for the non-chiral photonic crystals and are interpreted in both a Bragg scattering model and a photonic bandstructure model. A ‘GaAs’ and a ‘diamond’ basis are presented for the interference pattern with a 397 nm lattice constant. Photonic crystals have been fabricated with the ‘GaAs’ basis and evaluated by scanning electron microscopy.

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To Granny

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Chapter 1

Introduction

Photonic crystals, sometimes known as *photonic bandgap structures*, are dielectric microstructures, which are periodic in one, two or three dimensions with a periodicity of the order of the wavelength of light, and thus modulate electromagnetic radiation. The concept of a photonic bandgap was first proposed independently by both Yablonovitch [1] and John [2] in analogy to the electronic bandgap of semiconductors. A photonic crystal is the optical equivalent of an electronic semiconductor.

Much effort has since been expended on fabricating artificial photonic crystals, and the number of groups worldwide developing techniques to fabricate photonic crystals has mushroomed. As ever though, nature got there first. The beautiful iridescence of opals is a sign that these gems are in fact naturally occurring photonic crystals, formed in a sedimentary or volcanic environment when amorphous silica spheres stack to form a three-dimensionally periodic structure [3]. The iridescence of a natural opal, shown in figure 1.1, is due to the periodic microstructure of the material and is further enhanced by the inclusion of natural defects. Figure 1.2 shows a scanning electron micrograph of the periodic stacking of amorphous silica spheres in a natural opal. A further example of

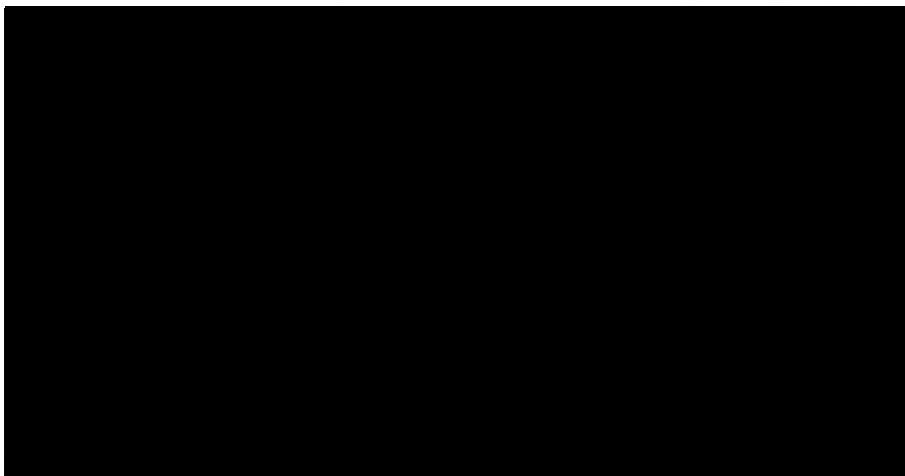


Figure 1.1: Natural opals are an example of a three-dimensional photonic crystal. Formed in a sedimentary or volcanic environment, they consist of close-packed amorphous silica spheres. *Image taken from www.lmbe.seu.edu.cn/~guzhz/photonic%20crstal/collection.html*

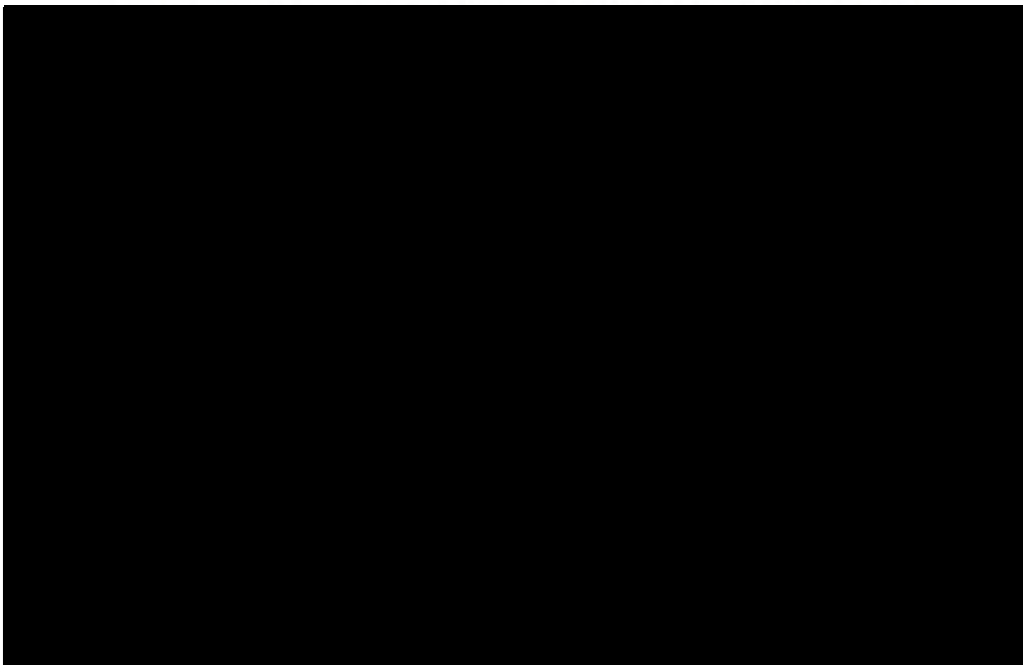


Figure 1.2: The scanning electron micrograph shows the periodic arrangement of the amorphous silica spheres, which form a natural opal. *Image taken from www.lmbe.seu.edu.cn/~guzhz/photonic%20crstal/collection.html*

a naturally occurring photonic crystal are the hairy spines on the sea-mouse, *Aphrodita* sp. (Polychaeta: Aphroditidae), which are shown in figures 1.3 and 1.4 [4, 5]. The spine walls have the same structure as a type of optical photonic crystal fibre developed by Russell [6]. Figure 1.5 shows a transmission electron micrograph of a cross-section of a seamouse spine and, for comparison, a scanning electron micrograph of the cross-section of a photonic crystal fibre is shown in figure 1.6. Further examples of photonic crystal structures found in biological systems such as butterfly wings or beetles can be found in [7].

Why the interest in photonic crystals? The optical phenomena which arise from the formation of bandgaps and the degree of control which photonic bandstructure gives over the propagation of light give rise to many exciting ideas for new device applications. Potential devices include low-loss waveguides and LEDs with high external efficiencies [8]. The most compelling reason for developing photonic bandgap structures is the potential for integrated optical chips. When two conductors cross, the original electronic signals cannot be recovered after the junction. Routing on electronic chips therefore becomes a three-dimensional problem. Since modern electronic chips typically contain millions of transistors, VLSI design is complex and expensive. Two light waves can however cross without destroying the original signals. Optical routing can therefore remain a two-dimensional problem, potentially making optical chip design easier and cheaper.

This thesis describes the fabrication of three-dimensional photonic crystals by *holographic lithography*, a technique developed in the groups of Profs. Turberfield and Denning [9], and the characterisation of these photonic crystals. I concentrate on two face-centred cubic structures, known as the 922 nm pattern, and the 397 nm pattern respec-

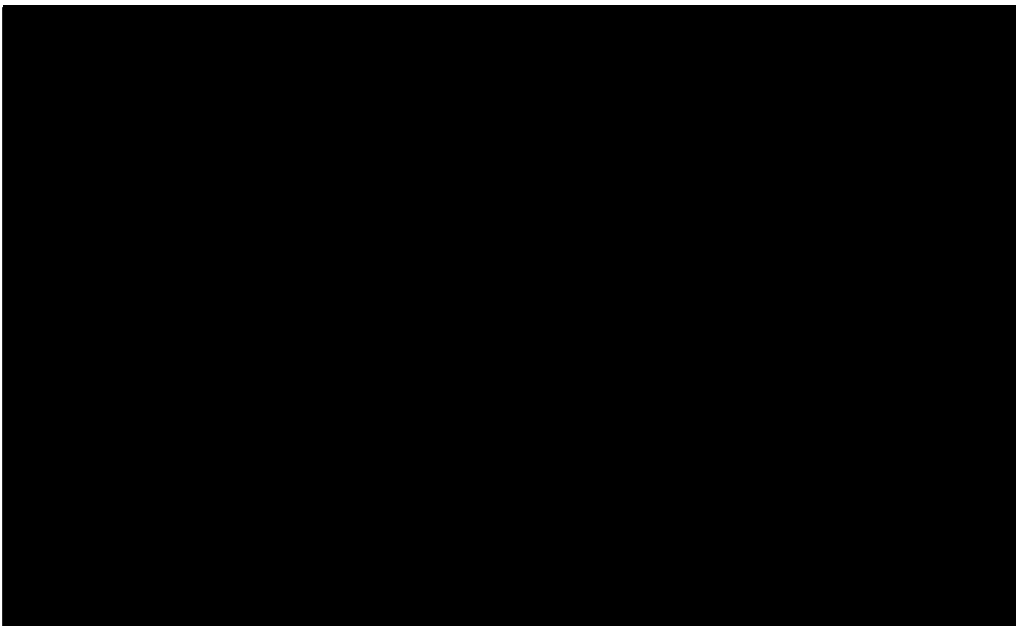


Figure 1.3: The sea mouse is covered in hairy iridescent spines, which are in fact photonic crystal structures. *Image by D. R. McKenzie 2002 School of Physics, University of Sydney. All rights reserved.*



Figure 1.4: The sea mouse spine is iridescent due to the photonic crystal structure of the spine. Different incident wavelengths of light are reflected at different angles. *Image by D. R. McKenzie 2002 School of Physics, University of Sydney. All rights reserved.*

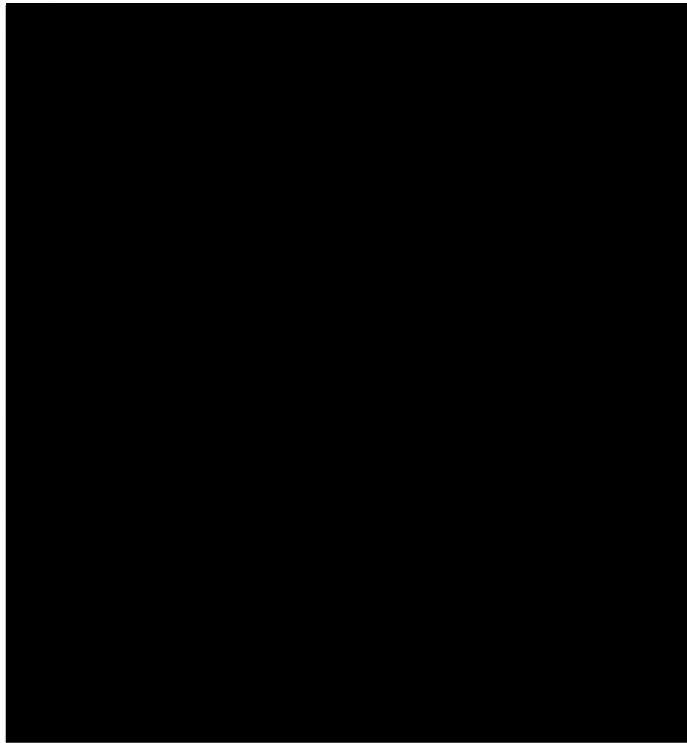


Figure 1.5: A transmission electron micrograph of a subsection of a sea mouse spine wall shows a honeycomb periodic structure, which is remarkably similar to that of the artificial photonic crystal fibres produced by Russell [6]. *Image by D. R. McKenzie 2002 School of Physics, University of Sydney. All rights reserved.*



Figure 1.6: The scanning electron micorgraph of a photonic crystal fibre shows the periodic hexagonal array of air holes with a central defect (a missing hole) which acts as the fibre's core. *Image taken from www.bath.ac.uk/physics/groups/opto/pcf.html*

tively¹. In chapter 2, I discuss photonic crystals in general. Section 2.1 covers the theory behind photonic bandgap formation. In section 2.2, I briefly discuss some of the physical consequences of photonic bandstructure and potential applications, and in section 2.3, I briefly review the techniques for fabricating three-dimensionally periodic microstructures.

In chapter 3, I discuss the fabrication of photonic crystals by holographic lithography. In section 3.1, I present the theory behind the formation of periodic interference patterns, and in section 3.2 the optical holographic set-up. The photoresist chemistry is described in section 3.3 and imaging of our photonic crystals by scanning electron microscopy in section 3.4. The processing steps are described in section 3.5. I give an overview of some adhesion techniques for adhering the photonic crystals to substrates in section 3.6.

In chapters 4 and 5, I cover the fabrication of photonic crystals with the 922 *nm* interference pattern and their characterisation by scanning electron microscopy and optical transmission measurements. In section 4.1, I describe the parameters required to generate a face-centred cubic interference pattern with a conventional cube side of 922 *nm* in air and show that we can produce either a chiral or a non-chiral basis. Chiral interference patterns and photonic crystals are discussed in greater detail in section 4.2. I show how to implement the 922 *nm* interference pattern in section 4.3 and present scanning electron micrographs of photonic crystals fabricated with this pattern in section 4.4. Chapter 5 deals with the optical characterisation of these photonic crystals. In section 5.1, I discuss the experimental set-up, which I constructed for measuring the optical transmission of the photonic crystals. The issue of sample orientation in the experimental set-up is addressed in section 5.2. The optical transmission spectra are presented in section 5.3 and interpreted in a Bragg scattering model. Some anomalous features in the transmis-

¹These labels refer to the lattice constants of four-beam interference patterns generated with a 355 *nm* laser wavelength.

sion spectra are discussed in 5.4. In section 5.5, I interpret the transmission data using photonic bandstructure calculations.

In chapter 6, I present a photonic crystal structure fabricated using a face-centred cubic interference pattern with a much smaller lattice constant and much wider calculated bandgap, the 397 nm interference pattern. In section 6.1, I describe the 397 nm interference pattern, and in section 6.2, how to fabricate photonic crystals with this interference pattern. Scanning electron micrographs of photonic crystal structures exposed to the 397 nm interference pattern are presented in section 6.3.

Finally, I briefly review the work presented in this thesis and discuss possible future directions for holographic lithography in chapter 7.

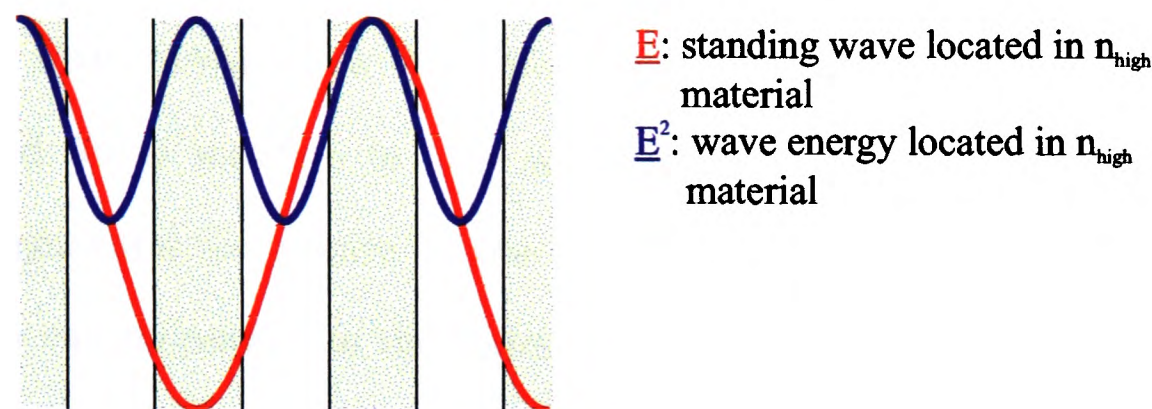
Chapter 2

Photonic Crystals

2.1 Photonic Crystals in Theory

Photonic crystals are periodic microstructures with a periodic variation of the dielectric constant in one, two or three dimensions. They are the photonic equivalent of natural crystals, and the analogy between electromagnetic (EM) wave propagation in a photonic crystal and electron wave propagation in a real crystal is a useful tool to develop a basic understanding of photonic bandgap formation. Concepts familiar from the nearly free electron model such as bandstructure, bandgaps, reciprocal space and Brillouin zone boundaries are routinely carried over to the EM case [10, 11].

The formation of photonic bandgaps can be explained by comparison to X-ray scattering. If the period of the modulation of the dielectric constant is of the order of the wavelength of light, i.e. submicron, then, providing the dielectric is not absorbing at the given photonic frequency, photons can undergo multiple scattering from the dielectric crystal planes inside the photonic crystal. Coherent scattering from periodically distributed scatterers in space (Bragg scattering) leads to the formation of photonic



1D periodic refractive index modulation

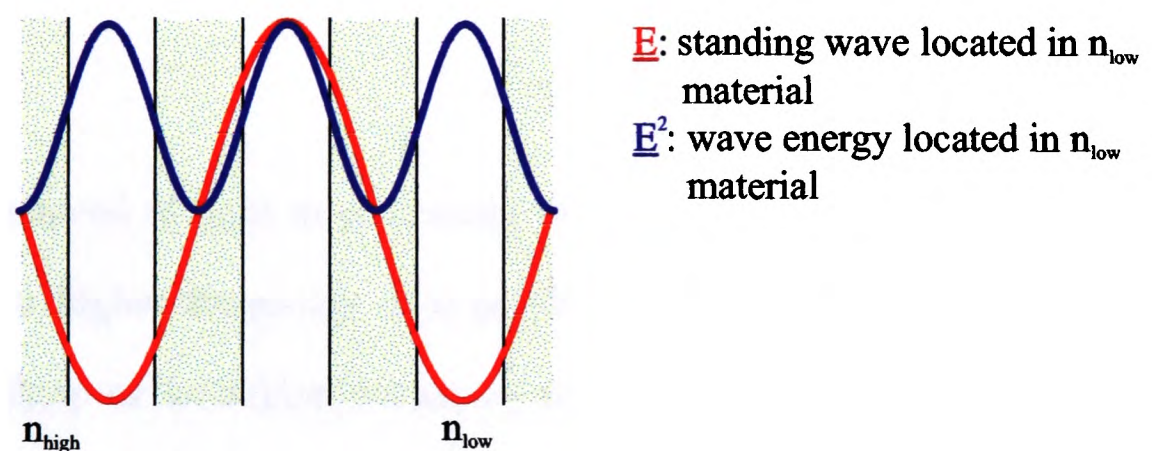


Figure 2.1: The incident and Bragg reflected EM waves interfere to form a standing wave with the wave energy concentrated in the regions of high dielectric constant. The standing wave energy can also be concentrated in regions of low dielectric constant. The energy difference between the two standing wave energies is the photonic bandgap.

bandgaps [12]. In X-ray scattering, the atoms in a crystal are weak scatterers of X-rays. In the case of a photonic crystal however, the dielectric ‘atoms’ are strong scatterers, which leads to larger bandgaps and greater distortions of the dispersion relations than one would expect to see in X-ray scattering.

For nodes with wavevector $\mathbf{k}$ at a Brillouin zone (BZ) boundary, the incident and Bragg-reflected waves interfere to form an EM standing wave. There are two non-degenerate eigenstates for a wave at the Brillouin zone boundary. The nodes of the standing wave can be centred in the regions with low dielectric constant, in which case the wave energy is concentrated in regions of high dielectric constant, ϵ_{high} , as shown in figure 2.1. In the second eigenmode, the wave energy is concentrated in regions of low dielectric constant, ϵ_{low} . From the equation

$$\omega = \frac{c |\mathbf{k}|}{\sqrt{\epsilon}} \quad (2.1)$$

where c is the speed of light in a vacuum, we can see that the wave in the low dielectric material has a higher frequency ω than the wave in the high dielectric material. A photonic bandgap or forbidden frequency region has opened up between the two wave modes [13], which is shown schematically in figure 2.2. Clearly, as the refractive index contrast ($\sqrt{\epsilon_{\text{high}}} : \sqrt{\epsilon_{\text{low}}}$) increases, the width of the frequency gap increases.

Crystals with a complete bandgap, where photons of a given frequency cannot propagate in any direction in the lattice, are of particular interest in order to take full advantage of the nature of photonic crystals. Let us therefore consider what happens when a plane wave propagates in two separate directions in a lattice, using the face-centred cubic (fcc) lattice for illustrative purposes. As I will discuss later on, the fcc lattice is particularly favourable for the formation of a complete bandgap. The first BZ boundary of a face-centred cubic lattice is depicted in figure 2.3 [10]. The origin of the zone is marked Γ . The

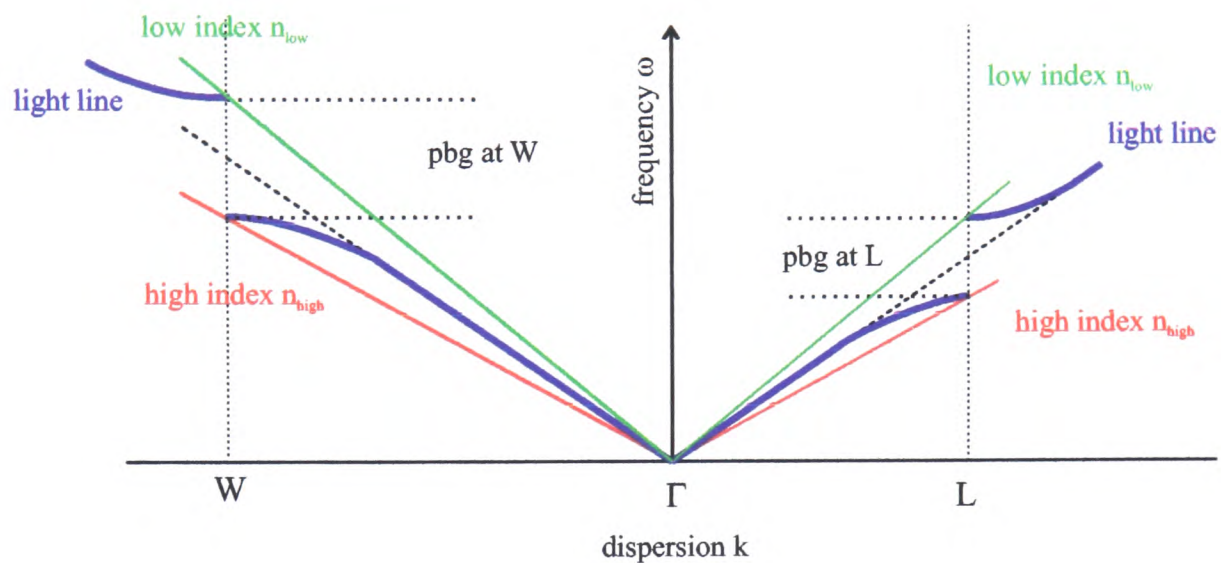


Figure 2.2: Schematic of a photonic dispersion curve. The crystallographic directions to the nearest (L) and the furthest (W) points on the first BZ boundary of the face-centred cubic lattice have been plotted on the dispersion axis. At the BZ boundary, the photonic band in the first BZ is pushed down towards the high dielectric dispersion curve; the photonic band in the second BZ is pushed up towards the low dielectric dispersion curve. A frequency band with no allowed propagating photonic modes opens up. The forbidden frequency gap at the BZ boundary in the ΓL direction is lower than the forbidden gap at the BZ boundary in the ΓW direction. To achieve a complete photonic bandgap, the two gaps must overlap.

BZ point closest to the origin is the L point ($|\Gamma\mathbf{L}| = \sqrt{3}\pi/a$, a is the lattice constant), the furthest point is the W point at the intersection of three planes ($|\Gamma\mathbf{W}| = \sqrt{5}\pi/a$). A forbidden frequency gap centred at ω_L or ω_W will form for plane waves travelling in the $\Gamma\mathbf{L}$ or $\Gamma\mathbf{W}$ directions respectively. As the dispersion plot in figure 2.2 shows, ω_L is lower than ω_W . The gaps at these two extremal zone-edge frequencies need to overlap to achieve a forbidden frequency band in both directions and hence in all directions. A complete photonic bandgap requires forbidden frequency overlap in all 4π sterad of reciprocal space.

The more symmetrical the BZ boundary, the closer together the extremal zone-edge frequencies are, and the lower the refractive index contrast needs to be for the frequency gaps to overlap. Of the Bravais lattices, the first BZ boundary of a face-centred cubic lattice, shown in figure 2.3, most closely resembles a sphere. The most favoured lattice geometries for the formation of a three-dimensional photonic bandgap are therefore based on the face-centred cubic lattice, as both Yablonovitch [1] and John [2] suggested in their initial proposals for the existence of photonic bandgap structures.

2.1.1 Bandstructure Calculations

There are several packages devoted to computing the dispersion relations or photonic bandstructures of optical systems.

We use the freely-available MIT Photonic-bands (MPB) software package¹ to compute the photonic bandstructure [14]. MPB adopts a frequency-domain approach: the eigenstates and eigenvalues of Maxwell's equations are calculated directly by iterating over approximate eigenstates, in a plane-wave expansion. The alternative approach is a

¹<http://ab-initio.mit.edu/mpb/>

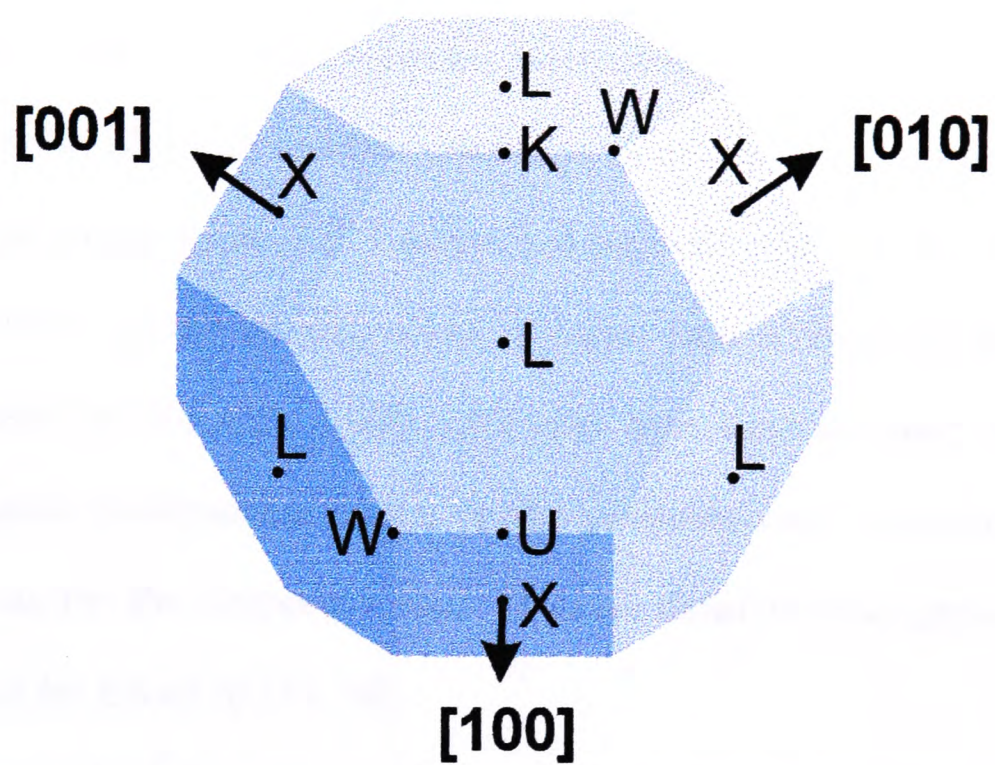


Figure 2.3: The first Brillouin zone boundary of a face-centred cubic photonic crystal. The high symmetry points are marked. The fcc BZ boundary is the most spherically symmetric of all Bravais lattices, which makes it the most likely candidate for a complete photonic bandgap.

time-domain one, where Maxwell's equations are iterated in time [14].

The MPB code requires as input the spatial distribution of the dielectric constant within the primitive unit cell of the structure to be computed. The MPB code outputs the energy eigenvalues as a function of wavevector components.

2.1.2 Plane-wave Expansion of Maxwell's Equations

To calculate the refractive index contrast which will result in a complete bandgap, we need to calculate the photonic bandstructures or dispersion relations by solving Maxwell's equations for the propagation of EM waves in a periodic dielectric lattice. It is important that the full vector nature of EM waves is taken into account in the calculations, as first demonstrated by Ho et al. [15]. We note here that we need to take account of the two orthogonal polarisation states in the photonic case in contrast to the scalar-wave calculations for the electronic case. A more detailed description of the following calculations may be found in [13, 16].

The following calculations are based on the plane-wave expansion of the magnetic field. The propagation of light in a photonic crystal is governed by the four Maxwell equations, which can be written in SI units as follows:

$$\begin{aligned} \nabla \cdot \mathbf{B} &= 0 & \nabla \wedge \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} &= 0 \\ \nabla \cdot \mathbf{D} &= \rho & \nabla \wedge \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} &= \mathbf{J} \end{aligned} \quad (2.2)$$

where $\mathbf{E}$ and $\mathbf{B}$ are the macroscopic electric and magnetic fields, $\mathbf{D}$ and $\mathbf{H}$ are the displacement and magnetic induction fields, ρ and $\mathbf{J}$ are the free charges and currents.

Most photonic crystals consist of a periodic dielectric material, with no free charges or currents ($\rho = \mathbf{J} = 0$), which is linear (ϵ and μ constant), has no magnetic susceptibility,

is isotropic ($\mathbf{D} = \epsilon \mathbf{E}$, $\mathbf{B} = \mu \mathbf{H}$) and lossless (ϵ real). This assumption considerably simplifies Maxwell's equations:

$$\begin{aligned}\nabla \wedge \mathbf{E}(\mathbf{r}) &= i \frac{\omega}{c} \mathbf{H}(\mathbf{r}) \\ \nabla \wedge \mathbf{H}(\mathbf{r}) &= -i \frac{\omega}{c} \epsilon(\mathbf{r}) \mathbf{E}(\mathbf{r})\end{aligned}\quad (2.3)$$

where $\epsilon(\mathbf{r})$ is the periodic, spatially varying dielectric constant, ω is the frequency, and c is the speed of light. We also ignore any explicit frequency dependency of ϵ .

These equations can be combined to form an eigenvalue equation for the magnetic induction, with eigenstates $\mathbf{H}_{\mathbf{k}}$:

$$\nabla \wedge \left(\frac{1}{\epsilon(\mathbf{r})} \nabla \wedge \mathbf{H}_{\mathbf{k}}(\mathbf{r}) \right) = \frac{\omega^2}{c^2} \mathbf{H}_{\mathbf{k}}(\mathbf{r}) \quad (2.4)$$

Since the dielectric constant $\epsilon(\mathbf{r})$ is periodic, we can expand it in a Fourier series:

$$\frac{1}{\epsilon(\mathbf{r})} = \sum_{\mathbf{G}} \kappa_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.5)$$

where $\mathbf{G}$ is a reciprocal lattice vector. Furthermore, Bloch's theorem can be applied and $\mathbf{H}_{\mathbf{k}}$ expanded in an infinite sum of plane waves:

$$\mathbf{H}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \mathbf{h}_{\mathbf{kG}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (2.6)$$

The transverse nature of $\mathbf{H}$ requires the vector amplitudes $\mathbf{h}_{\mathbf{kG}}$ to satisfy the zero divergence condition, $\nabla \cdot \mathbf{H} = 0$, which in turn implies that $\mathbf{h}_{\mathbf{kG}}$ are orthogonal to $\mathbf{k} + \mathbf{G}$. We can therefore introduce an orthonormal basis ($\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, (\mathbf{k} + \mathbf{G})/|\mathbf{k} + \mathbf{G}|$). The vector amplitudes can then be decomposed as follows:

$$\mathbf{h}_{\mathbf{G}} = h_{\mathbf{G},1} \hat{\mathbf{e}}_1 + h_{\mathbf{G},2} \hat{\mathbf{e}}_2 \quad (2.7)$$

and substituted into the eigenvalue equation to obtain the matrix equation:

$$\sum_{\mathbf{G}', \lambda'} H_{\mathbf{G}, \mathbf{G}'}^{\lambda \lambda'} h_{\mathbf{G}', \lambda'} = \frac{\omega^2}{c^2} h_{\mathbf{G}, \lambda} \quad (2.8)$$

where

$$H_{\mathbf{G},\mathbf{G}'} = \kappa_{\mathbf{G}-\mathbf{G}'} |\mathbf{k} + \mathbf{G}| |\mathbf{k} + \mathbf{G}'| \begin{pmatrix} \hat{\mathbf{e}}_2 \cdot \hat{\mathbf{e}}_{2'} & -\hat{\mathbf{e}}_2 \cdot \hat{\mathbf{e}}_{1'} \\ -\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_{2'} & \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_{1'} \end{pmatrix} \quad (2.9)$$

This eigenvalue problem must be solved numerically, using standard matrix diagonalisation techniques in order to obtain the dispersion relations $\omega(\mathbf{k})$. The plane wave expansion method is computationally expensive, which in turn constrains the accuracy of the calculation as the number of terms in the Bloch expansion must be restricted [17]. Sakoda quotes numerical errors exceeding 5% with the number of terms in the plane wave expansion exceeding 3000 [17].

The geometry of the basis and its connectivity also play an important role in the formation of a photonic bandgap. For a given lattice type, with a fixed lattice parameter and fixed refractive index contrast, the shape of the basis can have a big impact on the photonic bandstructure. For example, a face-centred cubic lattice with a basis consisting of a dielectric sphere can only exhibit a complete photonic bandgap if the refractive index contrast is > 2.85 [18]. If the symmetry of the structure is lowered however by replacing the single spherical ‘atom’ with a ‘two-atom’ basis consisting of two dielectric spheres just touching each other along the (111) direction (the ‘diamond’ structure), then a complete photonic bandgap can open up at lower refractive index contrasts. Calculations have shown that the ‘diamond’ structure appears to be most favourable for bandgap formation [19]. The lowest refractive index contrast resulting in a complete photonic bandgap found to date ($n = 1.87$) is for a ‘diamond’ lattice with nearest-neighbours connected by dielectric rods [20].

2.2 Motivation for Photonic Crystals

Why the interest in photonic crystals? Some of the optical phenomena which arise naturally from photonic bandstructures, and the degree of control which a photonic crystal enables over the propagation of light give rise to many exciting new device applications. In the following section, I will briefly outline some of these phenomena and some potential applications.

2.2.1 Spontaneous Emission

The ability to control spontaneous emission has great practical importance, and the possibility of controlling spontaneous emission was in fact one of the motivations behind the original proposals for a photonic bandgap structure [2, 21].

In a potential spontaneous emission event, if there are no optical modes available for an emitted photon to populate, then the spontaneous emission event will be suppressed. By suitably engineering the photonic bandgap structures, it is possible to design the density of available optical modes to control or inhibit spontaneous emission. For example, in direct gap semiconductors, the radiative recombination of an electron-hole pair could be prevented by incorporating the semiconductor in a photonic bandgap material in some way and engineering the photonic bandgap so that it straddles the electronic band edge. Figure 2.4 illustrates how a photonic bandgap can inhibit electron-hole recombination by eliminating any free optical modes for the emitted photon.

2.2.2 Self-collimating Phenomenon

Light propagating inside a photonic crystal can be self-collimating: the beam inside the photonic crystals can be collimated independently of the divergence of the incident beam,

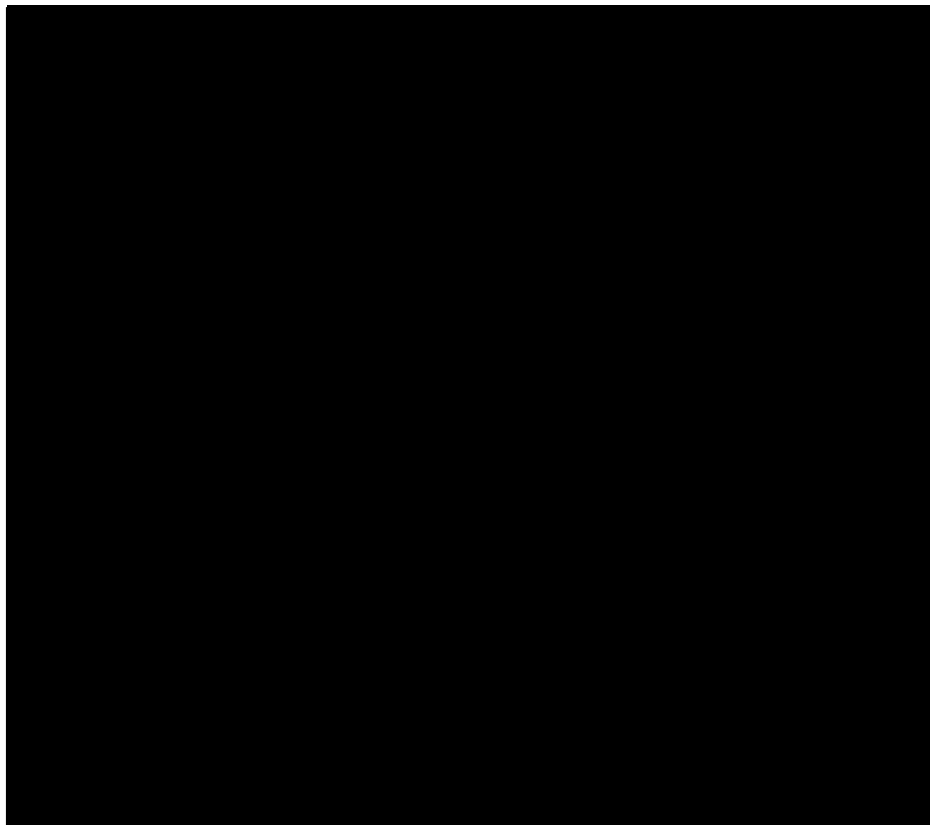


Figure 2.4: Electron-hole recombination with the associated emission of photons can be inhibited in a suitably engineered material. On the right-hand side, the photonic dispersion has been plotted with a forbidden photonic bandgap centred at $h\nu$. On the left-hand side, the electron wave dispersion typical of a direct-gap semiconductor has been plotted; the dots represent electrons and holes. The photonic bandgap has been designed to straddle the electronic band edge. As a result, electron-hole recombination is inhibited since no photons of frequency ν are allowed to propagate in the material due to the photonic bandgap. *Figure taken from [21].*

purely by taking advantage of the anisotropic dispersion surface of a photonic crystal [22]. Light inside a photonic crystal can similarly be made to converge or diverge.

The propagation of light inside the photonic crystal is determined by the dispersion surfaces of the crystal; the direction of propagation is normal to the dispersion surface [22]. By suitably designing the dispersion surfaces, it is possible to fabricate the photonic crystal equivalents of a collimator, a concave lens and a convex lens. Figure 2.5 shows how this might work in principle.

2.2.3 Superprism Effect

Superprism phenomenon is the term describing the highly angle-sensitive light propagation observed inside a photonic crystal [23]. A slight change in the angle of an incident beam (from $+7^\circ$ to -7°) has been shown to result in a large change of the light beam propagating inside a photonic crystal (from $+70^\circ$ to -70°), which is explained by a strong modification of the group velocity due to the anisotropy of the dispersion surface of the photonic crystal.

2.3 3D Fabrication Methods

Work on one- and, in particular, two-dimensional photonic crystals has been extensive, partly because it is easier to produce two-dimensionally periodic structures than three-dimensionally periodic structures. Techniques from the semiconductor processing industry have been very successfully adapted to create photonic bandgap structures in one and two dimensions. For example, standard electron beam and dry etching techniques have been used to produce a hexagonal array of air holes in GaAs [24]. A review of some of these techniques, such as lithography or electrochemistry, can be found in reference [8].

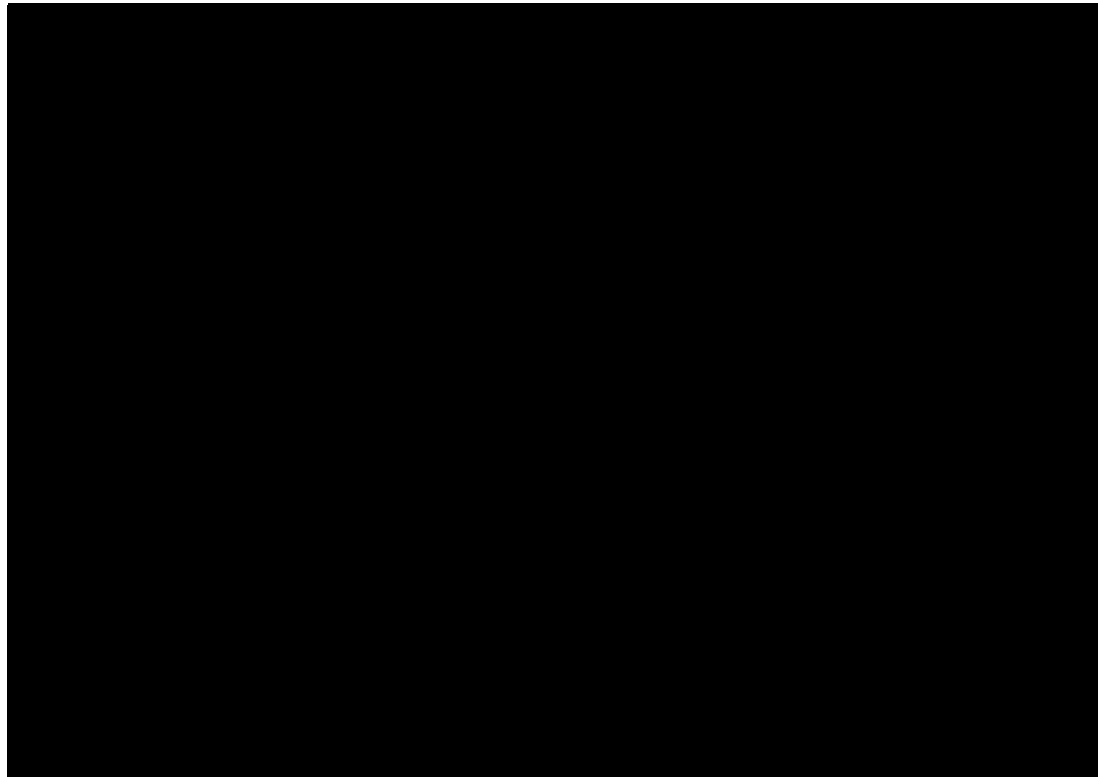


Figure 2.5: The schematic illustrates how a photonic crystal can be used as a concave lens (case A_1), a collimator (B) and a convex lens (A_2). The thick curve shows a typical branch of a photonic dispersion surface in reciprocal space. The arrows above the dispersion surface show the incident wavevectors in reciprocal space. The direction of propagation of the light in the crystal is normal to the dispersion surface. The arrows below the dispersion surface therefore indicate the energy flow in real space. By suitably choosing the curvature of the dispersion surface on which the light is incident, it is therefore possible to use a photonic crystal as either a collimator, a concave or a convex lens. *Image taken from [22]*

Imposing periodicity in three dimensions, particularly at optical wavelengths, has proved to be much more of a challenge. The challenge of producing large-scale structures with submicron periodicity in three dimensions stretches current fabrication techniques to the limit, but it is a challenge worth pursuing if the full potential of photonic bandgap structures is to be realised. Some of the techniques developed to fabricate three-dimensional photonic crystals are briefly reviewed in the following paragraphs.

2.3.1 Yablonovite

The first experimental demonstration of a photonic crystal with a complete bandgap in three dimensions appeared in 1991 [25]. This structure, now known as Yablonovite after its creator Eli Yablonovitch and shown in figure 2.6, has microwave periodicity and is fabricated by drilling a pattern of intersecting holes that form a face-centred cubic structure in a high refractive index material [21]. The drilling can be performed with a real drill bit to produce photonic bandgaps in the microwave spectrum or by reactive ion etching or X-ray lithography for the optical spectrum [26]. Engineered defects can be included by locally adding or removing material.

2.3.2 Techniques Adapted from the Semiconductor Industry

Techniques originally developed for the silicon microchip industry have been successfully adapted to build up photonic crystals in three dimensions.

This approach has been particularly successfully exploited by the group of Profs Lin and Fleming at Sandia National Laboratories, where a layer-by-layer stacking scheme is adopted to construct log-pile structures [27, 28, 29]. The structures are fabricated from silicon wafers using advanced techniques borrowed from micro-electro-mechanical

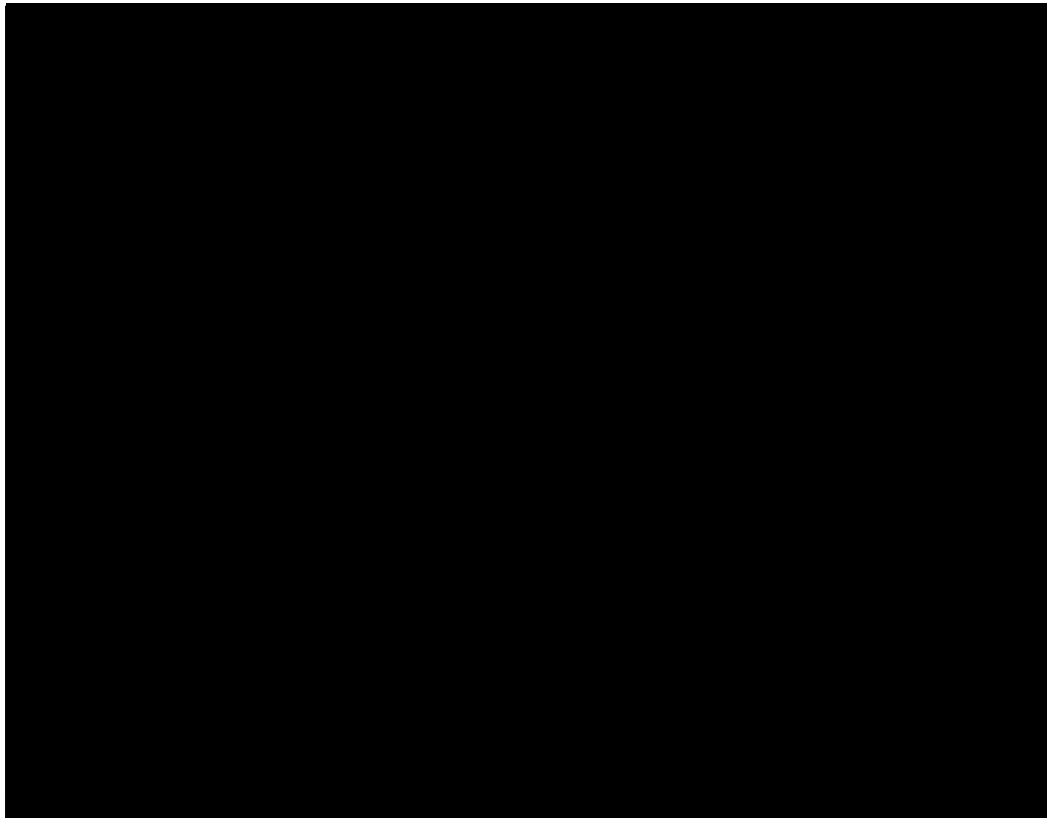


Figure 2.6: Yablonovite, the first artificial three-dimensional photonic crystal with a complete photonic bandgap in the microwave spectrum, was fabricated by drilling holes to form a face-centred cubic lattice in a volume of dielectric material and ensuring that the ‘atoms’ were non-spherical.

system (MEMS) fabrication and integrated circuit processing. Schematically, silicon rods, 180 nm wide, are photopatterned, etched and the spaces in between infilled with silicon dioxide (SiO_2). The process is repeated, according to the desired stacking sequence, until the required number of layers has been deposited. The SiO_2 is then removed by wet etching. The Sandia structure has a strong transmission dip in the near-infrared, centred at $1.6\text{ }\mu\text{m}$, covering the telecommunications window between $1.35\text{ }\mu\text{m}$ and $2.15\text{ }\mu\text{m}$.

The autocloning technique [30, 31] relies on the deposition of two kinds of dielectric film by bias sputtering on prepatterned substrates to produce three-dimensional periodic microstructures, composed of alternate Si and SiO_2 layers. Under certain conditions, the bias sputtering, a film deposition technique in which sputtering and sputter-etching take place simultaneously [30], preserves the corrugation of the substrate instead of flattening out the surface. Pattern integrity is maintained over many layers, typically 10 – 20 repeats of a Si/ SiO_2 pair. One layer of Si or SiO_2 is typically 200 nm thick, and the spacing between nearest-neighbour cells is 500 nm . The autocloning process is self-healing: aperiodic perturbations in the initial periodic shape of the pattern disappear over several deposition layers [32]. Drilling of cylindrical columns in the stacking direction by dry-etching leads to a structure geometrically similar to the diamond lattice with a complete photonic bandgap [33, 34].

The glancing angle deposition (GLAD) method [35, 36] has been adapted to fabricate tetragonal square spiral photonic crystals [37, 38]. In a single processing step, a semiconducting material such as silicon is deposited by physical vapour deposition on prepatterned substrates at extremely high angles of incidence ($80^\circ - 90^\circ$). At these angles, the incident flux of material only deposits on raised prepatterned regions. Growth is restricted to these regions, and self-shadowing continues to restrict growth to these

regions as the structures grow. At regular intervals, the substrate is rotated by 90° to introduce right-angle bends in the growing columns, which gives the structures their square helical characteristic. The pitch of the helix, typically 1300 nm , is determined by the time elapsed between rotations of the substrate. The side length of the square cross-section of the helix is determined by the pitch and the deposition angle, typically 700 nm for 85° deposition angle. The side length of the square cross-section of the rod itself, typically 440 nm , is determined by the deposition angle and the seed density.

Wafer fusion techniques with ingenious alignment methods have been used to produce unit cells of log-pile structures in semiconductors. For example, semiconductor plates can be patterned in two dimensions, using conventional integrated circuit processing techniques, and then robotically stacked, using polystyrene microspheres in locating holes to achieve the required three-dimensional periodicity [39]. Controlled defects can also be incorporated using this micromanipulation method. Alternatively, prepatterned two-dimensionally periodic semiconductor wafers are stacked robotically and aligned using a laser beam diffraction pattern [40, 41, 42]. Again, controlled defects can be introduced into the structures with this methodology. Diamond-type structures have also been fabricated by robotic stacking of silica microspheres [43], which gives good control and also enables defects to be included, but is limited so far to very small samples.

2.3.3 Self-Organising Systems

Much research has focussed on self-organising systems that self-assemble into large scale photonic crystals with three-dimensional periodicity. An extensive review of three-dimensional photonic crystals fabricated by self-assembly methods can be found in reference [44].

Colloidal crystals are grown from concentrated suspensions of monodisperse particles such as polystyrene beads [45, 46], latex beads [47] or silica [48, 46] spheres (artificial opal), which naturally sediment into a face-centred cubic lattice. The lattice constant can be varied simply by engineering the diameter of the spheres [49], typically ranging from 200 *nm* to 700 *nm*. Face-centred cubic colloidal crystals do not in general have the required connectivity or refractive index contrast (≥ 2.85 [18]) to produce a complete photonic bandgap [50, 51]. The inverted opal structure, where the face-centred cubic structure is templated with a higher refractive index material and the template removed in some fashion, does however have a complete photonic bandgap, providing the refractive index contrast is sufficiently high (e.g. a complete bandgap opens up between the eighth and ninth band for a refractive index of 3.6 and fill fraction of air to material of 0.78 [52]). Colloidal crystals are therefore used as templates by infiltrating them with higher index materials such as cadmium sulfide (CdS) [53] and cadmium selenide (CdSe) [54] nanocrystals to form arrays of quantum dots, CdS and CdSe to form crystalline inverted-opal type structures [55] by electrochemical deposition, nanoparticulate silicon [56], titania [57, 47] by sol-gel chemistry and carbon [58] by chemical vapour deposition.

Defects such as stacking faults or dislocations are difficult to eliminate in self-assembled systems. Since the bandgap opens up between higher frequency bands, it does not survive even small perturbations of the crystal lattice [52]. Template-directed colloidal growth can minimise the recurrence of such unintentional defects [59]. It also enables the deliberate introduction of air-core line defects [60]. It is also possible to control the sedimentation process and self-assemble single-crystal silicon arrays directly onto a substrate such that the bandgap survives in the inverted structure [18].

2.3.4 Optical and Holographic Techniques

Several groups have used optical scanning techniques to produce three dimensional photonic bandgap materials. Log-pile stacks and tapered waveguide structures have been fabricated by scanning a tightly focused Ti:Sapphire laser and using two-photon initiators to photopolymerise acrylates [61] or inorganic-organic hybrid materials [62] to enhance the resolution of the resulting structures. The resolutions achieved (individual rods with a diameter of 200 nm and spacing between the rods of 250 nm) make these photonic crystals suitable for optical applications. Log-pile stacks of aluminium oxide with a lattice constant of $66\text{ }\mu\text{m}$ have also been fabricated by laser chemical vapour deposition [63]. In principle, any geometry can be produced using such methods, so long as the structure holds together. Engineered defects can also easily be introduced into the crystals. Alignment of successive layers and shrinkage can however be problematic over large scales.

Log-pile stacks have also been built layer-by-layer by writing holographic gratings in successive layers of AsScTc chalcogenide glasses, which are photosensitive and have high refractive indices [64].

Holographic lithography, a technique first developed in the group of Profs. Turberfield and Denning [9, 65], is a flexible and appealing method for producing microstructures with three-dimensional periodicity in photosensitive materials in a single processing step. Photosensitive polymer is exposed in a single pulse to a laser interference pattern with three-dimensional periodicity to produce large-scale microstructures.

Jakšić [66] independently suggested using volume interference patterns in a photosensitive medium such as dichromated gelatin to fabricate photonic bandgap structures. The two-dimensional principle was also proposed independently by Berger [67, 68]. Since our

group's demonstration of holographic lithography [9], several other groups have realised the potential of this technique and have fabricated photonic bandgap structures similar to ours [69, 70, 71].

Periodic structures in a photoresist have been fabricated by interfering spatially coherent extreme ultraviolet light from a Synchrotron Radiation source [72].

Shoji and Kawata [73] have also used laser interference techniques to fabricate three-dimensionally periodic microstructures in photopolymers. Unlike holographic lithography, this method is a two-step process in which the resin is exposed first to a two-dimensionally periodic interference pattern to produce an array of rods and then to a one-dimensionnal grating pattern, orientated orthogonally to the rods. The resulting structures have three-dimensional connectivity of material, but only two-dimensional connectivity of the voids. A combination of two lenses and a diffractive beam splitter have been used to create femtosecond laser interference patterns and produce three-dimensional photonic crystals [74]. No polarisation control of the beams however leads to poor periodicity in the direction of the optic axis. This will be discussed further in section 3.1.

The optical and holographic techniques discussed so far have all used negative photoresists, i.e. regions of high intensity correspond to material in the exposed structure. A volume interference pattern has been suggested as an 'optical drill' for the fabrication of three-dimensional photonic crystals in positive photoresists [75].

Chapter 3

Fabrication of 3D Photonic Crystals by Holographic Lithography

Holographic lithography is a very flexible technique and can be used to produce periodically patterned microstructures with sub-micron periodicity in one, two or three dimensions. The technique simply consists in patterning a film of photoresist with a periodic interference pattern. Two monochromatic plane waves can be interfered to produce an interference pattern which is periodic in one dimension — a grating. If three plane waves are interfered, then, if the differences between their wavevectors are non-collinear, the intensity distribution is periodic in two dimensions. Our structures, which are periodic in three dimensions, are formed by interfering four beams with non-coplanar wavevector differences. In regions of high intensity, the photoresist polymerises and is rendered insoluble. So long as the low intensity regions, the ‘voids’, interconnect, the unpolymersed photoresist can then be washed out in solvent. The polymerisation threshold is a function of the photochemistry. The resulting 3D photonic crystal may be processed in a number of ways.

In this chapter, I describe how holographic lithography is put into practice. In section 3.1, I discuss the theory behind interference patterns. In section 3.2, I describe the optical set-up. In section 3.3, I discuss our choice of photoresist and its chemistry and in section 3.4, a method of imaging structures by scanning electron microscopy. In section 3.5, I describe the fabrication of photonic crystals, and in section 3.6 various adhesion techniques designed to produce flat films suitable for optical transmission measurements.

3.1 Holographic Lithography in Theory — Definition of Lattice and Basis

The geometry of the crystal is determined primarily by the intensity distribution of the interference pattern in the photoresist. We therefore need to control the interference pattern in order to control the geometry of the structures. The optical interference pattern is determined by the intensity distribution at the intersection of the four coherent laser beams, which can be readily calculated. Such optical lattices have been studied in some depth by groups investigating atom-trapping [76, 77].

In general, the electric field in the i_{th} ($i = 1, 2, 3, 4$) beam can be written as:

$$\begin{aligned} \mathbf{E}_i &= \epsilon_i e^{i(\mathbf{k}_i \cdot \mathbf{r} + \phi_i)} \\ &= \epsilon_i \hat{\mathbf{p}}_i e^{i(\mathbf{k}_i \cdot \mathbf{r} + \phi_i)} \end{aligned} \quad (3.1)$$

where $\mathbf{k}_i$ is the wavevector, ϕ_i is the phase, ϵ_i is the field amplitude, and $\hat{\mathbf{p}}_i$ is the polarisation unit vector. The total electric field at the intersection of the four beams is equal to the vector sum of the four individual beams:

$$\mathbf{E} = \sum_{i=1}^4 \epsilon_i e^{i(\mathbf{k}_i \cdot \mathbf{r} + \phi_i)} \quad (3.2)$$

and the intensity distribution in the resist is proportional to the square of the electric field:

$$\begin{aligned}
 I \propto \mathbf{E} \cdot \mathbf{E}^* &\propto \sum_{i=1}^4 \sum_{j=1}^4 \boldsymbol{\epsilon}_i \cdot \boldsymbol{\epsilon}_j^* e^{i((\mathbf{k}_i - \mathbf{k}_j) \cdot \mathbf{r} + (\phi_i - \phi_j))} \\
 &\propto \sum_{i=1}^4 \sum_{j=1}^4 \epsilon_i \epsilon_j \hat{\mathbf{p}}_i \cdot \hat{\mathbf{p}}_j^* e^{i(\Delta \mathbf{k}_{ij} \cdot \mathbf{r} + \Delta \phi_{ij})}
 \end{aligned} \tag{3.3}$$

This equation is remarkably similar to the equation describing the intensity distribution of x-rays scattered by a polyatomic crystal [10].

The wavevector differences may alternatively be written in the following format:

$$\Delta \mathbf{k}_{ij} = \mathbf{G}_{ij} \tag{3.4}$$

where $\mathbf{G}_{ij}$ represent reciprocal lattice vectors. By analogy with the electronic crystal, the exponential factor in identity 3.3 thus may be considered as the lattice form factor. The expansion coefficients $\boldsymbol{\epsilon}_i \cdot \boldsymbol{\epsilon}_j^*$ are determined by the polarisation vectors and the field amplitudes of the four beams. By analogy with the atomic form factor described in Ashcroft [10], it is clear that these prefactors determine the shape of the basis. The intensity distribution of the optical lattice can be rewritten in a simpler and more intuitive fashion as follows:

$$I(\mathbf{r}) \propto \sum_{i,j=1}^4 S_{ij} e^{i(\mathbf{G}_{ij} \cdot \mathbf{r} + \Delta \phi_{ij})} \tag{3.5}$$

where S_{ij} represents the structure factor.

With four interfering beams, there are just three independent relative phase differences, $\Delta \phi_{12}$, $\Delta \phi_{23}$ and $\Delta \phi_{34}$. A phase shift in any one of the beams merely translates the optical lattice in space.

$$I(\mathbf{r} - \mathbf{r}_0) \propto \sum_{i,j=1}^4 S_{ij} e^{i(\mathbf{G}_{ij} \cdot \mathbf{r} - (\mathbf{G}_{ij} \cdot \mathbf{r}_0 - \Delta \phi_{ij}))} \tag{3.6}$$

$$\propto \sum_{i,j=1}^4 S_{ij} e^{i(\mathbf{G}_{ij} \cdot \mathbf{r} - \Delta \phi'_{ij})} \tag{3.7}$$

where $\Delta\phi'_{ij} = -(\Delta\phi_{ij} - \mathbf{G}_{ij} \cdot \mathbf{r}_0)$ is a constant. The three independent phase components essentially fix the spatial position of the origin of the optical lattice. For the purpose of determining the geometry of the interference pattern, the phase components play no role and are set equal to zero.

The translational symmetry of the interference pattern depends on the Fourier components $\mathbf{G}_{ij}$, of which there are thirteen in a four-beam interference pattern (the terms $S_{ii} e^{i(\mathbf{G}_{ii} \cdot \mathbf{r} + \Delta\phi_{ii})}$ are constants). As long as the Fourier components $\mathbf{G}_{ij}$ ($i \neq j$) are non-coplanar, we can choose any three as primitive basis vectors of a three-dimensional reciprocal lattice. All Fourier components of the interference pattern lie on this reciprocal lattice. The four-beam interference pattern is thus necessarily periodic in three dimensions. It is in fact possible to describe any of the fourteen three-dimensional Bravais lattices [78, 79, 80] by suitably choosing the four wavevectors. We choose a set of primitive basis vectors $\mathbf{G}_{1j}$ ($j = 1, 2, 3, 4$) of the reciprocal lattice corresponding to the desired real-space lattice, then find the reciprocal vector $\mathbf{q}$ equidistant from the origin and $\mathbf{G}_{1j}$. The wavevectors are then $\mathbf{q}$ and $\mathbf{q} - \mathbf{G}_{1j}$. There are an infinite number of primitive basis sets for a given Bravais lattice, which will generate interference patterns of that Bravais lattice with, in general, different lattice parameters.

It is important and fundamental to point out that it is not possible to choose an arbitrary shape for the basis, given the limited number of Fourier components (a maximum of four beams interfere). Once the polarisation vectors and amplitudes in the four beams have been fixed, the shape of the basis can easily be calculated. The inverse process is not straightforward though. In other words, it is not necessarily possible to calculate the polarisation vectors and relative intensities which would produce a particular basis [78]. In principle, the number of available Fourier components could be increased by interfer-

ing five or more laser beams, which in turn would widen the range of achievable basis shapes. However, introducing extra beams introduces additional independent wavevector differences, which must correspond to reciprocal lattice vectors of the original four-beam lattice else we could end up with a superposition of two non-commensurate lattices (such a situation is shown in figure 4.15).

In summary, the wavevectors determine the lattice of the interference pattern, the polarisation vectors and relative amplitudes the basis.

It is important to visualise the interference patterns before creating the structures. In particular, we are looking for three-dimensional connectivity of the material so that the developed structure does not simply fall apart. The voids also need to be interconnected to ensure that unpolymerised material can be washed out by the developing solvent. The intensity distribution at the intersection of multiple beams in a volume is calculated using the Interactive Data Language (IDL), an array-based language developed by Research Systems Incorporated.

One particularly useful feature of IDL is its capability to render constant-intensity surfaces in a volume efficiently and to slice through such surfaces, allowing us to examine possible interference patterns before fabricating the structures. In practice, we compare the constant intensity surfaces with scanning electron micrographs of photonic crystal surfaces. If we make the implicit assumption that the photoresist is a negative one (c.f. section 3.3), then high intensity areas inside the constant intensity surface correspond to polymerised material; the low intensity areas, the voids, correspond to areas where the photoresist remains unpolymerised. The polymerisation intensity threshold of the photoresist, which corresponds to the constant intensity surface, is a function of several variables, which will be discussed in chapter 3.5.2.

Since our overall aim is to fabricate photonic crystals with a complete three-dimensional bandgap, we want to calculate the photonic bandstructure of any interference pattern. This is easily achieved by simply inputting an isosurface of an interference pattern produced in the IDL calculations directly into the MPB code (described in 2.1.1). We can specify high-symmetry reciprocal lattice vectors at which we require the bands to be calculated; the code will interpolate a specified number of reciprocal lattice vectors in between these points. Furthermore, we can specify the number of bands to be calculated at each reciprocal lattice vector.

An interesting problem is the initial choice of parameters, in particular the choice of polarisations and relative intensities for the four beams. To ensure three-dimensional connectivity of both material and void in the developed structures, the basis needs to vary relatively slowly across the unit cell. As discussed in depth in [79], this is only the case if the non-zero Fourier components lie near the origin of the reciprocal lattice. Once the wavevectors have been fixed to generate a particular Bravais lattice, the search space for polarisations, linear, circular or elliptical, and relative intensities remains infinitely large. Once a choice of parameters has been made, the contrast of the interference pattern (ratio of maximum and minimum intensities) needs to be examined. The photochemical reaction during and after exposure is equivalent to setting an intensity threshold: in regions above this intensity threshold the photoresist polymerises, in regions below this intensity threshold the photoresist remains unpolymerised and is dissolved away. The higher the intensity contrast, the easier it is to fabricate the desired photonic crystal. When a low-contrast interference pattern was used in [69], the photoresist had to be designed to compensate for the uniform background intensity.

The approach adopted in our group looks for highly symmetrical solutions, since this

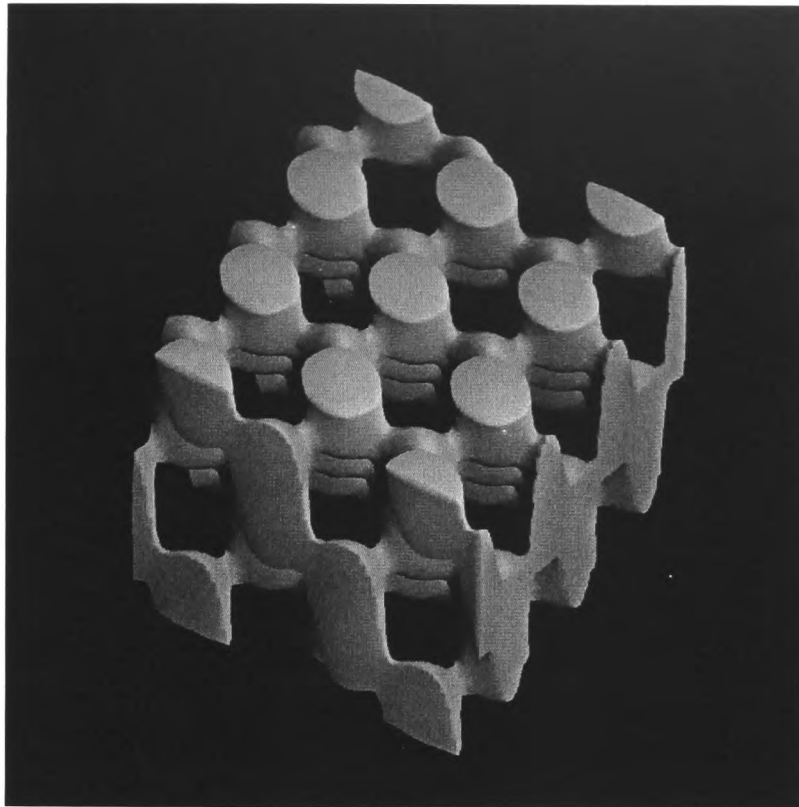


Figure 3.1: An iso-surface of a face-centred cubic interference pattern with a conventional cube side of 922 nm in air when the interference wavelength is 355 nm .

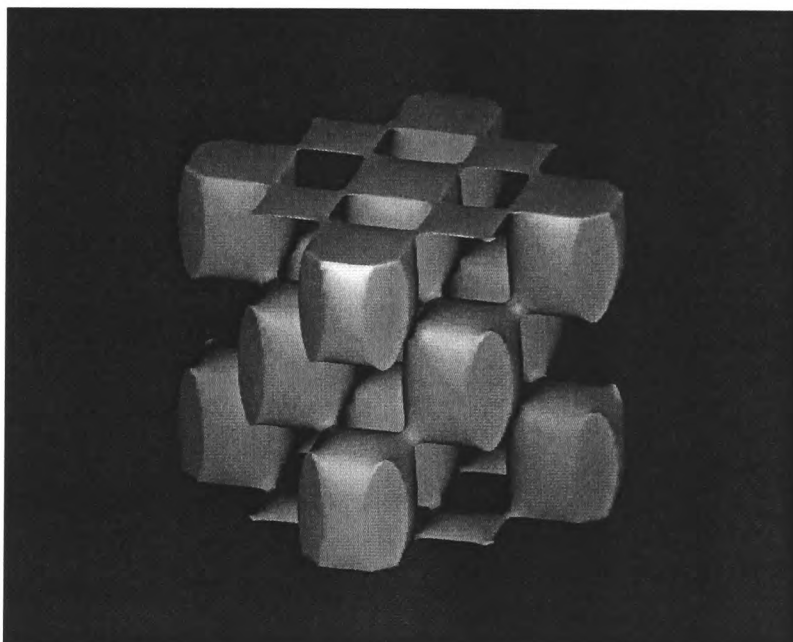


Figure 3.2: An iso-surface of a face-centred cubic interference pattern with a conventional cube side of 397 nm in air when the interference wavelength is 355 nm .

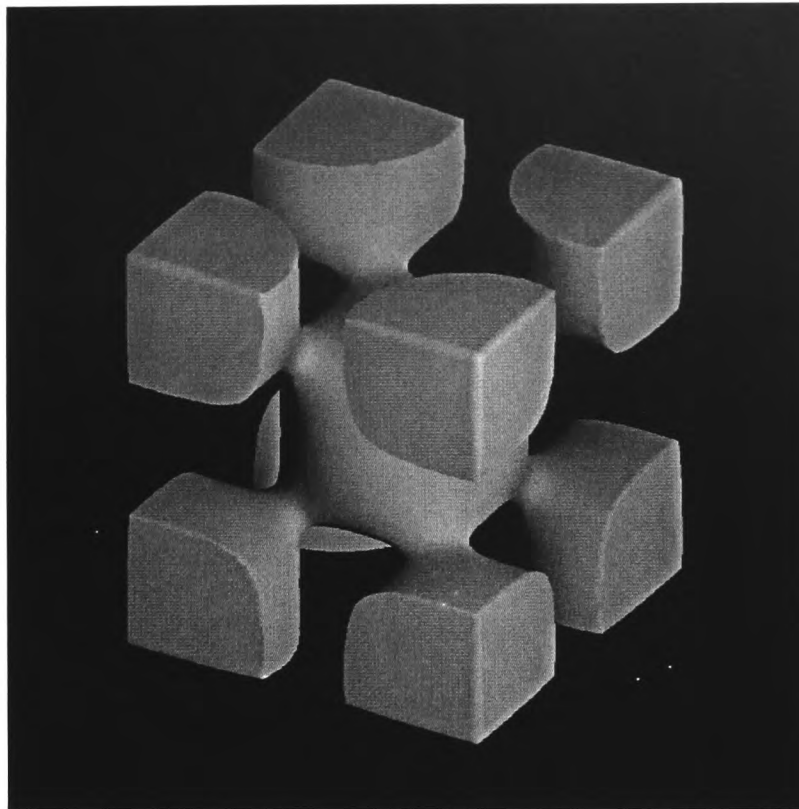


Figure 3.3: An iso-surface of a body-centred cubic interference pattern with a conventional cube side of 307 nm in air when the interference wavelength is 355 nm .

approach considerably simplifies the task. A number of highly symmetric interference patterns have been identified and reported by Sharp [78]. These include face-centred cubic structures with a conventional cube side of 922 nm , shown in figure 3.1, or 397 nm , shown in figure 3.2, and body-centred cubic structures with a conventional cube side of 307 nm , shown in figure 3.3, with the interference wavelength of $\lambda = 355\text{ nm}$, which we use, and in air. This thesis will concentrate on two such interference patterns, the 922 nm face-centred cubic pattern described in chapter 4 and the 397 nm face-centred cubic pattern described in chapter 6.

3.2 Optical Holographic Set-up

We use a frequency-tripled, injection-seeded, Q-switched Nd:YAG laser (model Quanta Ray PRO-190-10), manufactured by Spectra Physics. The laser wavelength is 355 nm , close to the 365 nm mercury (Hg) line used in standard lithographic techniques [81], which enables us to adapt already proven photochemical techniques to our application. Mirrors, beamsplitters and waveplates are of multilayer dielectric design to minimise losses. Polarising beamsplitter cubes, Brewster windows, beamsplitters and waveplates are made from ultraviolet (UV) grade fused silica with antireflection coatings optimised for 355 nm . All optics are supplied by CVI Laser and are designed specifically for high-power UV laser applications. Although the beam itself is in the UV and therefore invisible to the human eye, we can monitor the beam quality by observing the fluorescence on a piece of white card, which is standard practice.

3.2.1 Choice of Laser

3.2.1.1 Optomechanical Stability

The photoresist is exposed in a single pulse, which is selected by a mechanical shutter situated at the laser exit port. The Q-switched laser pulse duration is 6 ns . Exposing the films in a single, short, very high-power (300 mJ per pulse) laser pulse reduces the need to worry about the mechanical stability of the optical components as well as the stability of the laser. Furthermore, the pulse duration is short compared to the physical and chemical processes initiated by the exposure pulse, reducing perturbations to the interference pattern by photoinduced changes to the refractive index of the photoresist.

3.2.1.2 Mode Quality of the Laser

Clearly, the mode quality of the laser pulse, both longitudinal and transverse, is very important to the quality of the structures.

In principle, the laser has been optimised by the manufacturers to give a transverse Gaussian beam distribution in the far-field. The optics are therefore laid out to give a long beam path, 6.47 m , from the shutter to the target. In order to obtain high-power output in a Gaussian-shaped beam with a relatively large diameter ($\approx 8\text{ mm}$), an unstable resonator design is employed [82]. As a result of the large beam diameter, diffraction from intra-cavity apertures is significant and degrades the transverse mode. This is visible as a series of concentric bright and dark rings, which, unfortunately, are rendered to some extent in the exposed structures as concentric rings of exposed and under-exposed material. Imperfections in the optics further degrade the beam quality. The amount of scatter visibly increases along the beam path. We have tried cleaning up the mode quality by spatial frequency filtering the beam. Although this does clean up the beam exiting from the spatial frequency filter, the beam quality degrades as it passes through further optics. Ideally, we would spatial frequency filter the beam as one of the last steps before the target, but this is not practical due to lack of space. In practice, the background scatter does not affect the film quality so long as the amount of energy diffused in the scatter is lower than the threshold required for polymerisation in the films.

Good longitudinal or temporal coherence of the laser beam is essential for holography. As has already been explained, a Q-switched pulse provides a short, high-power laser pulse, which sidesteps any problems associated with mechanical vibrations of the optics and hence avoids problems with blurring of the interference pattern. However, the coherence length of the laser pulse needs to be taken into consideration. In normal, unseeded,

Q-switched mode, the gain medium is pumped in a low Q-state (high loss cavity) until the upper laser level population density has reached its maximum potential [82]. The quality factor of the cavity is then switched to a high Q-state, allowing the cavity to lase and amplifying random spontaneous decays. The random nature of this process results in a laser pulse with a large number of temporal intensity spikes and short longitudinal coherence [83]. In injection-seeded, Q-switched mode, the stimulated emission cascade is initiated with a high-quality, narrow-linewidth, diode-pumped, continuous-wave Nd:YAG seed-laser, which is matched in wavelength to a longitudinal mode of the Q-switched cavity. The injection-seeded, Q-switched pulse is smooth and temporally coherent over its entire length [83].

We operate the laser at maximum power output where the laser is at its most stable. Any energy surplus to the application is then dumped externally.

3.2.2 Optical Layout

The laser beam is split four ways, and the path lengths of the four beams are equalised to within a couple of centimeters. A spatial mismatch in path lengths of two centimeters corresponds to a temporal mismatch of 70 ps , which corresponds to roughly 1% of the pulse duration and has a correspondingly small effect on the contrast of the interference pattern.

The wavevectors, the polarisation vectors and the relative intensities in the four beams determine the interference pattern, and these variables therefore need to be controlled separately in each beam. The final optics in each beam path are mounted on plates or ‘guns’. The guns in turn are mounted onto posts via rotation stages, which allows us to adjust both the height of the guns and the angles of the guns. The position of the

gun posts on the table along with the height and angle of the guns completely determine the wavevectors. The final optics in each gun consist of a half waveplate followed by a polarising beam splitter cube, both mounted in rotation stages. This combination allows us to control both the linear polarisation vector of the beam and the absolute intensity separately in each beam. If circular polarisation is required, a quarter waveplate in a rotation stage can be mounted after the beamsplitter cube. These optics are placed last to maintain the polarisation state at the target.

A Perspex block acts as a mount for the quartz disk acting as a substrate for the photoresist and as a beam dump for the surplus energy in the exposure laser pulse.

3.3 SU-8 Chemistry

We use a negative, epoxy-based, near-UV photoresist, known as EPON SU-8, which was designed specifically for ultrathick, high-aspect-ratio MEMS- type applications [84, 85, 86, 87]. The SU-8 monomer, shown in figure 3.4, consists of eight epoxy groups, which makes it readily cross-linkable and ideally suited for the fabrication of high connectivity three-dimensional structures. This potentially dense network of bonds leads to good solubility contrast between highly and weakly exposed material and produces a hard, glassy epoxy on exposure.

The photoresist is prepared by dissolving the monomer in an organic solvent, γ -butyrolactone (GBL), and adding a photoacid generator (PAG) as photoinitiator sensitive to the exposure wavelength of 355 nm . We use a triaryl sulfonium salt as the photoacid generator. The resist is then spun onto substrates using a conventional spin coater. Before exposure, the resulting thin film undergoes a series of processing steps, described in chapter 3.5.2, which drive off the solvent, leaving behind a hard glassy film of monomer

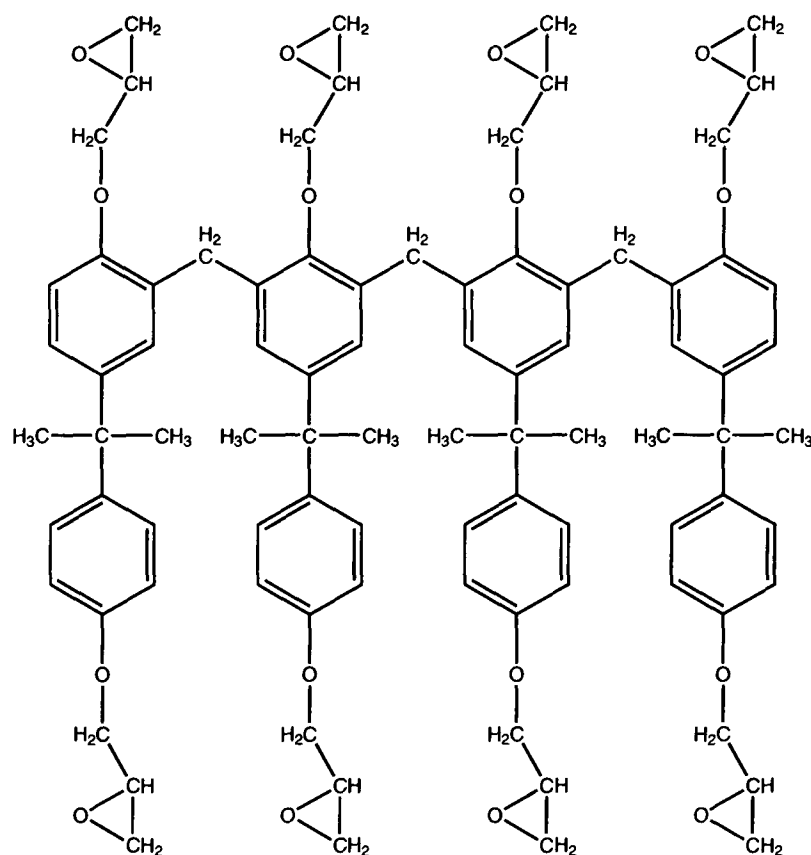


Figure 3.4: The SU-8 monomer contains eight epoxy groups for crosslinkage. This leads to high connectivity, which results in good solubility contrast between highly and weakly exposed material.



Figure 3.5: During exposure, a molecule of photoacid generator in the photoresist can absorb one UV photon, releasing a proton and sideproducts in a process known as Lewis acid photogeneration. This results in a latent pattern of protons, which is commensurate with the original exposure pattern.

solids.

The exposure and polymerisation stages are decoupled. SU-8 has low absorption at 355 nm so, as long as the films are optically thin, only the PAG absorbs significant amounts of energy from the interference pattern during exposure. A molecule of PAG can absorb one UV photon, releasing a proton and sideproducts as shown in figure 3.5 [88]. This results in a latent, inert pattern of photogenerated protons, whose density corresponds to the intensity of the original exposure pattern. If the films are stored in suitable conditions (low temperatures and low light levels), the proton pattern will remain unperturbed for weeks. The acid-catalysed polymerisation chain reaction, shown schematically in figure 3.6, is initiated by heating the resist just above the glass transition temperature of SU-8 ($T_g \approx 50^\circ\text{C}$ [89]). The glass transition temperature of amorphous polymers is the temperature at which the polymer moves from its glassy to its viscous state; the big monomer chains start to move freely relative to each other. This enables the protons to attack the polar O atom in the epoxy rings. This initiates a chain reaction as the epoxy rings open up and crosslink with each other, which is shown schematically in figure 3.6.

SU-8 is a negative photoresist: areas exposed to UV light are rendered insoluble; unexposed or weakly exposed areas remain soluble. Positive photoresists, where the exposed material is rendered soluble, are also in use, but will not be discussed any further here.

The commercially available resin also contains a large number of impurities, visible as brownish-yellow inclusions, and has a bright yellow appearance, which is unexpected given that the absorption coefficient of pure SU-8 decreases continuously from 10^2 m^{-1} to 1 m^{-1} between 400 nm and 800 nm [90]. We currently filter the resist through Nylon

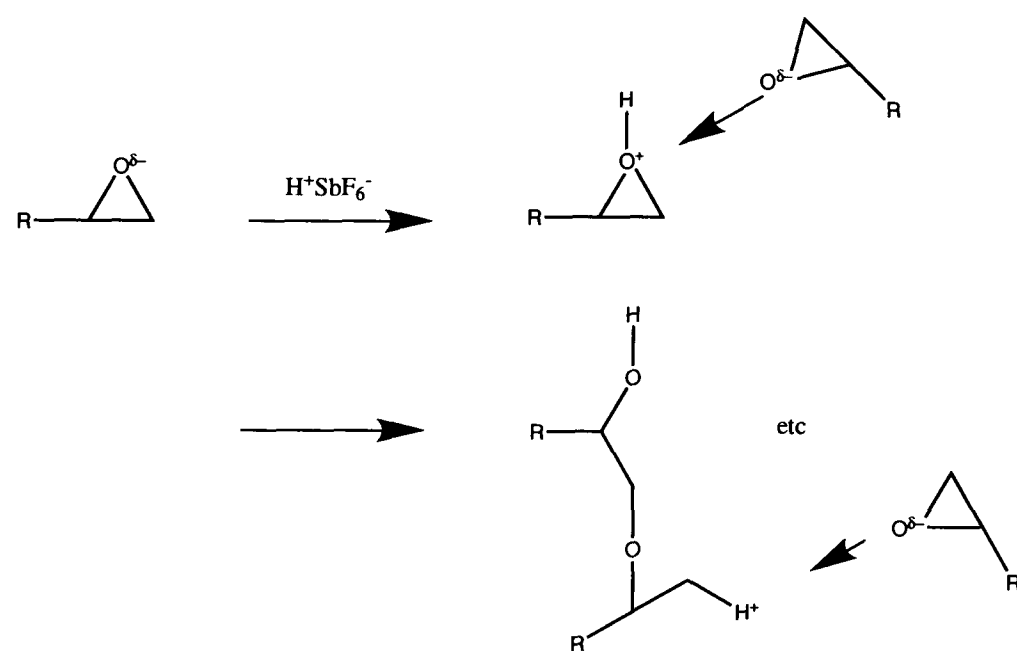


Figure 3.6: The acid-catalysed polymerisation chain reaction of SU-8 is shown schematically. The polar O atom in an epoxy ring of a single SU-8 molecule, represented by R, attracts a proton, forming a hydrogen bond. A polar O atom from a second SU-8 molecule in turn reacts with the positively charged initial epoxy ring, breaking it open and forming a crosslink. This sequence repeats itself until the chain reaction runs out of accessible epoxy groups or is quenched.

filters with micron-sized pore diameters: the majority of impurities are removed, but not the component responsible for the yellow appearance. Mass spectrometry further shows that the resin contains lighter and heavier oligomers, which are not necessarily readily incorporated into the crosslinked network. Work is ongoing in the group to either purify the SU-8 resist or develop an alternative epoxide-functional monomer. The current resist is more than adequate for fabricating well-defined homogeneous crystals up to $\sim 15 \mu m$ thick. In practice, the absorption coefficient of SU8 is 50 cm^{-1} ; the absorption coefficient of the PAG is $300 \text{ wtfraction}^{-1} \text{ cm}^{-1}$ and its quantum efficiency 0.4–0.5. The quantum efficiency of the PAG decreases with time and is dependent on storage conditions. This implies that in a photoresist with a 1% PAG concentration, one UV photon is absorbed by SU8 for every three photons absorbed by the PAG. There is scanning electron microscopy (SEM) evidence that absorbance at 355 nm becomes non-negligible in thicker films (the films are ‘optically thick’), causing depth-dependent structural changes in the crystals.

Clearly, the photoresist is a critical factor in determining the quality of the final structures. The introduction of air bubbles into the resist during its preparation is a major source of problems. Figure 3.7 shows an SEM image of a $\sim 400 \mu m$ diameter air bubble in a film spun with frothy resist, which is clearly not suitable for fabricating a photonic crystal. Unfortunately, it is hard to avoid introducing bubbles into the resist. The resin is not easily dissolved in GBL in high concentrations, and we find that we need to heat the GBL whilst stirring for a long time, which is the first significant source of bubbles. The second source occurs during filtering: forcing the viscous resist through the pores of the filter introduces further bubbles. Some steps can be taken to reduce the frothy quality of the resist. A cycle of heating the SU-8–GBL mixture to render it more fluid and then pumping on it in a vacuum chamber reduces the number of bubbles.

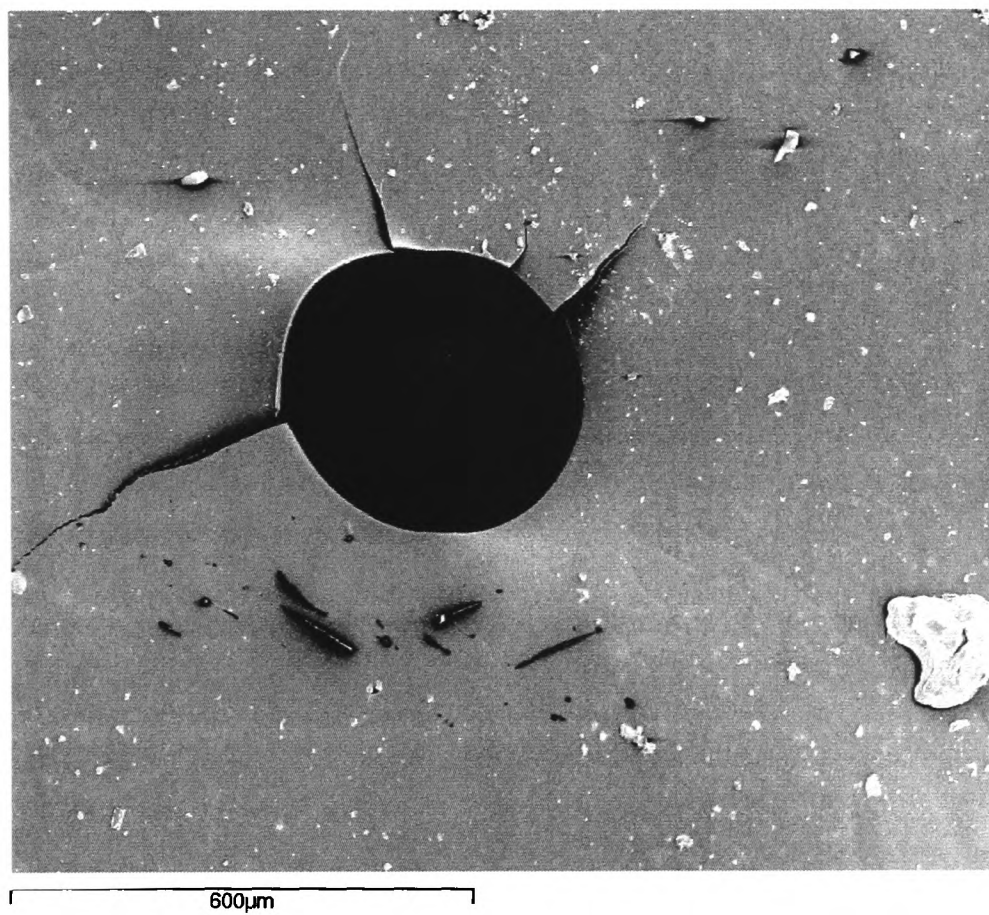


Figure 3.7: The scanning electron micrograph shows a $\sim 400 \mu m$ diameter hole in a film of polymerised SU-8 due to air bubbles in the resist, which makes the film unsuitable for the fabrication of a photonic crystal.

3.4 Imaging by Scanning Electron Microscopy

Photonic crystals fabricated by holographic lithography are expected to have sub-micron features, which can be imaged by electron microscopy. I use a JEOL JSM6300 scanning electron microscope¹. The electron gun consists of a single crystal of LaB₆ (lanthanum hexaboride) with a maximum achievable resolution in high contrast samples of $\sim 6\text{ nm}$.

As the polymeric samples are insulating, some preliminary preparation is required before they can be imaged in the electron microscope. The samples are mounted on aluminium stubs using electrically conductive, double-sided adhesive carbon disks. The samples are then sputter-coated with a thin film of gold, also a good conductor, which improves imaging and prevents charging of the specimen during imaging. The sputter-coater is a Biorad E5400 sputter-coater, in general use for gold plating of SEM specimens. The thickness of the coating is typically of the order of 5 nm ; the gold grains have a typical diameter of 10 nm , but can go up to 100 nm in poor conditions. These figures put an upper bound on the resolution of the features we can image. If necessary, the resolution can be increased by replacing gold with platinum (platinum grain diameters are typically smaller, actual sizes will depend on the coating system). Sputter-coating is not a line-of-sight deposition method; the formation of most artificial surface features such as ridges, which arise from directional coating, is therefore avoided, although some shadowing can, and does, occur.

The electron microscope was used in secondary electron imaging mode. In this mode, the high energy electrons interact with the loosely bound conduction band electrons in the coating. The amount of energy imparted to the secondary electrons is small. The

¹I wish to thank the Materials Department, University of Oxford, for kindly allowing me to make use of their microscopes.

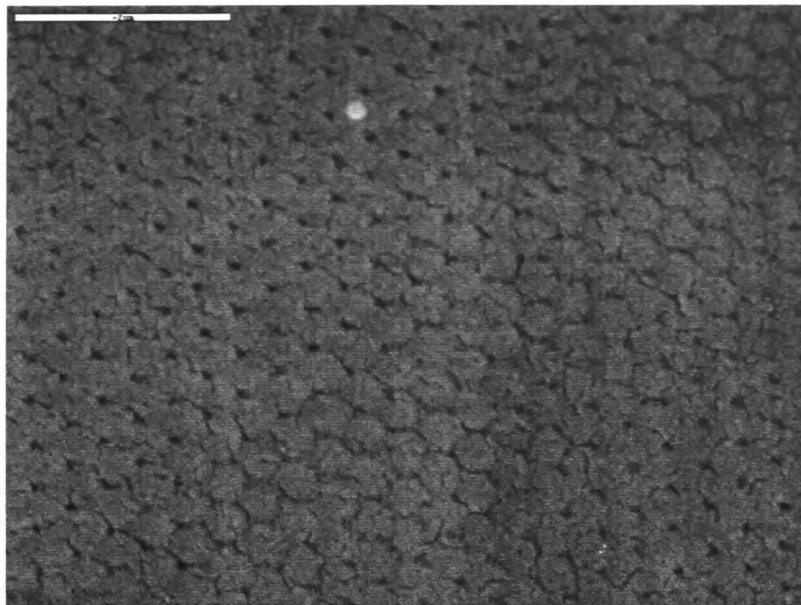


Figure 3.8: The scanning electron micrograph shows individual gold grains in a poor sample coating. The grain size ($\sim 100\text{ nm}$) limits the achievable image resolution.

scattering range in the samples is then small, of the order of a few nm . This technique is therefore ideally suited for imaging surfaces with sub-micrometer topographical features. In high-contrast samples, the best resolution achievable is about 6 nm at an acceleration voltage of 30 kV . This level of resolution is unachievable in the JSM6300 because of sample charging when the acceleration voltage is $> 10\text{ kV}$. Furthermore, the grain size of the gold particles in the coating can limit the achievable resolution. Figure 3.8 shows a scanning electron micrograph of individual gold grains in a poor sample coating, where the gold grains have a diameter of $\sim 100\text{ nm}$.

Features across the depth of a structure can be examined by fracturing the film and mounting it on an angled SEM stub, then preparing in the normal way. We are thus able to image cleavage planes as well as the film surface.

3.5 Fabrication of Photonic Crystals by Holographic Lithography

The fabrication process of a photonic crystal by holographic lithography is described in detail in this section.

3.5.1 Substrate Preparation

The photoresist is spin-coated onto UV-grade fused silica disks, which have been polished to a surface flatness of one wavelength per *cm*. The disks are 2 *mm* thick and measure 20 *mm* across. They are ideally suited for our purposes as they are robust, easy to handle with tweezers and can be reused. The substrates are transparent to the exposing beams and approximately index-matched to the photoresist (refractive index of fused silica: $n = 1.47$ at 355 *nm*; refractive index of SU-8: $n = 1.63$ at 355 *nm*). This minimises reflections at the film-substrate interface, which would otherwise perturb the interference pattern. The substrates are also approximately index-matched to the Perspex target with a mineral oil.

The resist is spun onto substrates with a conventional spin coater. The concentration of solids to solvent determines the viscosity and hence the film thickness. I typically prepare a resist concentration of 50% solids to GBL by weight, which corresponds to a film thickness of about 12 μm with a spin speed of 1000 rpm. I use a triaryl sulfonium salt as the photoacid generator (PAG) in a concentration of 1% by weight.

Substrate preparation is critical in order to achieve good quality, flat films for exposure. The disks are dusted with dry air, wiped with acetone and then optics-grade methanol before being baked for six hours at $\sim 450^\circ\text{C}$. The purpose of this bake is to

drive off any adsorbed water and to render the substrate surface hydrophobic in order to match the surface energy of SU-8 more closely [87]. When spin-coated onto a hydroxylated silica surface, the photoresist does not wet the surface properly, but retracts and forms irregular, lens-shaped films. Refraction into such films badly distorts the interference pattern.

Untreated silica surfaces tend to be hydroxylated [91]. The silica surface can be dehydrated simply by baking. Adsorbed water evaporates relatively rapidly for six to ten hours after the temperature has been raised and then at a much slower rate. Good surface coverage by the SU-8 photoresist is consistently observed when the substrates are baked for six hours at a temperature of $\sim 450^\circ\text{C}$, which corresponds to a surface density of hydroxyl groups of about 2 per nm^2 [91].

3.5.2 Film Preparation

I have adapted the SU-8 processing procedure suggested by the commercial SU-8 supplier Microlithography Chemical Corporation (MCC), which is shown schematically in the flow diagram in figure 3.9.

The resist is dispensed with a pipette and spin-coated onto the substrates with a conventional spin coater. A wide range of thicknesses is achievable, ranging from 750 nm to $450\text{ }\mu\text{m}$ [85]. Desired film thicknesses range from $12 - 15\text{ }\mu\text{m}$, which are achievable with a spin speed of 1000 rpm and a resist concentration of 50% solids by weight. In thicker films, absorption by impurities in the photoresist become significant, resulting in modification of the structure through the thickness of the film. In a post-application bake (PAB), the GBL solvent is slowly driven off by baking the films on hotplates for 5 min at the glass transition temperature of SU-8, $\sim 50^\circ\text{C}$, and then for 15 min at 90°C . This

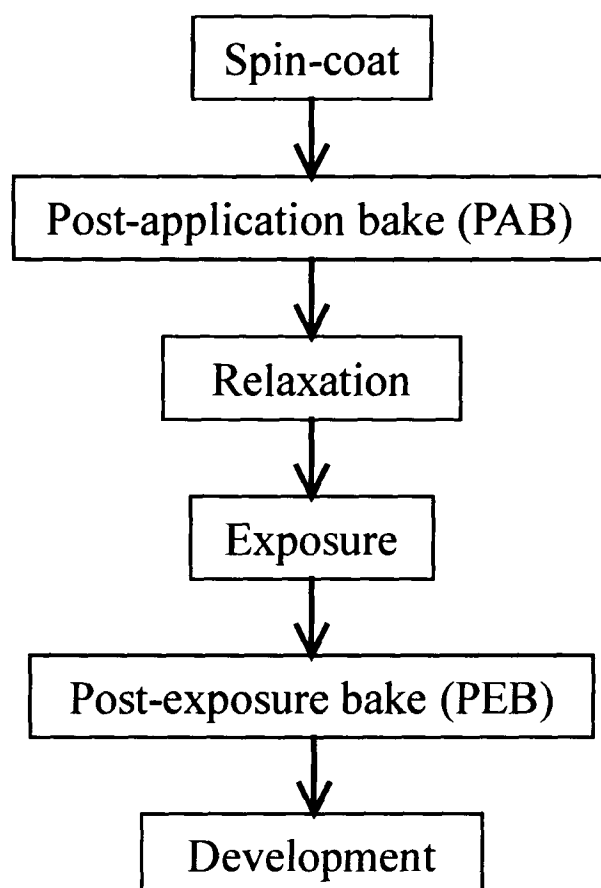


Figure 3.9: The flow diagram shows schematically the major steps in the fabrication of a photonic crystal by holographic lithography.

temperature is well below the boiling point of GBL (204°C) so the solvent evaporates slowly. It is important that the resist is heated gradually to prevent solvent vapour bubbles forming in the layer nearest to the heat source and erupting through the film. If the lower temperature bake is omitted, the film surface is marred by many craters, formed by collapsing solvent bubbles. Heating the films above the glass transition temperature serves two purposes. The flow of resist removes the characteristic lip at the edge of the spun film as the resist flows over the edge of the substrate. It is therefore very important that the hotplates are precisely leveled so that the film thickness remains constant. The flow of monomer also helps the solvent to evaporate. It is important to heat from below, i.e. on a hot plate, to prevent a 'skin' of hardened SU-8 from forming on the surface, significantly slowing further evaporation.

The films need to be cooled down below the glass transition temperature, and all

solvent driven off to maintain structural resolution by preventing any flow of the proton pattern after exposure. The films are cooled on a metal block, which acts as a heat sink. Once the films have cooled down, a simple, but reliable test, shows if all the solvent has been driven off. If the film surface feels tacky to the touch, then the residual concentration of solvent is too high, and the film needs to be baked at 90°C for a further length of time. The films are left to cool for 15 *min* at least in order to allow any stresses introduced during the PAB to relax by monomer chain rearrangement [86].

The films are exposed to the laser interference pattern in a single shot with an exposure dose of $\sim 120 \text{ mJ/cm}^2$, releasing a latent three-dimensional pattern of protons commensurate with the laser interference pattern. The pulse duration is much shorter than the timescales involved in the photochemical processes, so the interference pattern is unperturbed by changes in the refractive index due to the high intensities.

In a post-exposure bake (PEB), polymerisation is initiated by baking the films at a temperature just above the glass-transition temperature. Optimum structural resolution is obtained with a PEB of 2 *min* at 62°C. The films are plunged immediately into a bath of propylene glycol methyl ether acetate (PGMEA) to quench the polymerisation chain reaction. PGMEA acts as a developing agent by dissolving SU-8 monomer and partially cross-linked polymer. The structure, in a large volume of PGMEA, is fully cleared out in an ultrasonic bath heated to 40°C. Heating the developing solvent close to the glass transition temperature of the unexposed resin promotes the dissolution of the monomer. It is important at this juncture that the voids in the structure be interconnected so that the monomer can be fully cleared out and the required refractive index modulation achieved. Although there is a danger that weakly-crosslinked structures and structures with a low fill fraction fragment in the ultrasonic bath, the structures are not fully

developed in depth if sonication is omitted.

During development, the structures become detached from the substrates and float freely in the PGMEA. In the final processing step, the films are removed from the solvent and dried. PGMEA acts as a plasticiser, so if the films are removed directly from PGMEA and air-dried, the structure collapses. The films are therefore fished out on SEM particle analysis grids, rinsed a final time in clean PGMEA and then in isopropyl alcohol (IPA), which renders the structures more rigid. The photonic crystals can then be safely removed with tweezers and air-dried.

The top, where the interference pattern is incident on the film, and bottom surfaces of the structures cannot inherently be distinguished when imaged in the scanning electron microscope. During development the films detach freely from the substrates. When the dried films are mounted on SEM stubs, statistically 50% are mounted with the top surface facing up and 50% with the bottom surface facing up.

In solvent, the developed photonic crystals are very iridescent with beautiful reflected colours. They are flexible, thin films of plastic about 0.7 *cm* in diameter. When removed from the solvent, the stresses introduced into the structure by patterning and polymerisation cause the structures to shrink inhomogeneously. Often the structure in the laser beam profile is visible on the surface of the dried films. Furthermore, as the IPA solvent evaporates, surface tension at the phase boundary causes the films to curl at the edges and wrinkle. The dried films are brittle and uneven with a milky, opalescent appearance.

Critical point drying is a method developed to dry fragile biological specimens, which frequently collapse under the forces imposed by surface tension during air drying, by reducing surface tension to zero. Using liquid CO₂ as the transitional fluid, some promising initial results have been achieved when drying the samples using critical point drying:

the samples appear flatter and smoother on the surface. Further work is in progress to develop the parameters required to maintain the integrity of the three-dimensional structure.

One major appeal of the holographic technique is the non-linear post-exposure chemical amplification of the interference pattern, which imposes a sharp solubility interface on the continuously varying intensity distribution, resulting in a fully cross-linked robust periodic microstructure. The polymerisation threshold is determined by the number density, absorption cross-section and quantum efficiency of the PAG, by the exposure intensity as well as by the PEB temperature and duration, which determine the chain length and branching ration of the polymerisation chain reaction. For a given crystal geometry, there are four parameters at our disposal, which determine the fill fraction or ratio of material to void: the PAG concentration and exposure dose, post-exposure baking temperature and post-exposure baking time. The art of achieving of achieving good structural resolution lies in balancing these parameters so that the cleared out structure has good connectivity and basis resolution without closing off the pores.

Most of the energy in the exposure dose is deliberately dumped in the Perspex target to minimise depth attenuation of the interference pattern, and hence depth modulation of the structural resolution, by absorption in the photoresist.

The PAG concentration determines the fine resolution of the structure. To resolve a particularly complicated basis, the number density of initiator sites per basis needs to be higher than for a simple basis structure at the expense of increased absorbance across the depth of the structure. The PEB time can then be reduced to prevent overpolymerisation in a structure with a higher density of initiator sites. The PEB temperature is fixed just above the glass transition temperature of the monomer to prevent the flow of resist during

the postbake and maintain maximum structural resolution.

There is some evidence that the current exposure parameters produce a structure which just holds together and that the network of crosslinks is not fully developed. This is seen when GBL, a more aggressive solvent, which dissolves partially cross-linked SU-8, is used as a developing agent instead of PGMEA. The structures are then partially destroyed. Work is ongoing at the moment to add a base to the photoresist, which would mop up protons in weakly-exposed areas and prevent overpolymerisation if the PEB time were increased to allow the network to fully crosslink.

3.6 Flat Films

For optical measurements it is imperative that the samples be flat over the area being probed (typically an area of $\sim 600 \mu m^2$). Furthermore, for technical applications, e.g. in optical devices, it is necessary for the photonic crystals to be both flat and adhered to a substrate. For templating purposes, it would also be desirable if the photonic crystals could be attached to a range of substrates at will.

In the standard processing procedure, the structures, somewhat to our surprise, do not adhere to the fused silica disks they are processed on. As I described in section 3.5.2, the cross-linked films lift away from the substrate during development and float freely in the developing solvent. This is contrary to most SU-8 users' experience as polymerised SU-8 tends to adhere strongly to most substrates. MIMOTECH, an SU-8 supplier, even offered a prize to the first person to demonstrate dissolution of cross-linked SU-8 as the removal of SU-8 masks in lithographic processes is a major issue². The strains introduced into the system by polymerisation-induced shrinkage are a well-known source of wafer-

²<http://aveclafaux.freesevers.com/SU-8.html#top>

bowing when the thicknesses of the substrate and the polymer layer are comparable [86]. In our case, the silica substrates are much thicker (2 mm) than the polymer layer (12 μm), so the strains in the system can only relax when the film peels away from the substrate, which starts to happen as soon as the film is quenched in the developing solvent. Furthermore, only a small area of polymerised SU-8 is actually in contact with the substrate. Essentially, the developed microstructure consists of many little ‘feet’ which are in contact with the substrate. During agitation in the ultrasonic bath, the structure is literally shaken off the substrate.

Several methods for promoting adhesion of epoxy-based photoresists to silica can be found in the literature. These methods all rely on the deposition of an epoxy-based adhesion layer, which, on the one hand, binds well to silica and, on the other hand, reacts with the epoxy rings of the photoresist. Epoxy-based adhesion promoters, specifically tailored to SU-8 applications, are now commercially available³.

Several epoxy-based coating were tried in the hope of producing a flat film bonded to a substrate. Curiously, the films only successfully stick to SU-8 pre-coatings; no other epoxy-based coatings were successful in promoting adhesion. In section 3.6.1, I describe a technique which successfully bonds fully developed structures to microscope coverslips after the structures have become detached from their original silica substrates during development. In the remaining sections in this chapter, I describe silanisation, pulsed plasma deposition and alternative SU-8 coating techniques, which failed to bond the structured film to the adhesion layer.

³<http://www.somisys.ch/>

3.6.1 SU-8 as an Adhesion Promoter

Unpatterned, fully polymerised films of SU-8 stick strongly to silica, so it is appealing to use SU-8 itself as an adhesion promoter between the patterned films and the substrates.

Patterned films are fabricated and developed in the usual way, then attached to the adhesion layer (described below). By fabricating and developing the photonic crystals in the usual way, we ensure that a robust, well-defined structure is produced. Furthermore, the development stage clears out the remaining monomer and photogenerated protons. This prevents any acid diffusion occurring during the adhesion step, which could result in an overpolymerised photonic crystal. Alternative versions of this adhesion technique, which in many ways are more elegant and involve, for example, exposing the film directly onto the adhesion layer, result in overpolymerised structures. I will describe these alternatives in section 3.6.2).

The adhesion layer consists of a thin film ($< 2 \mu m$) of SU-8 photoresist, spun onto a microscope coverslip (*Best* 1.5 with a specified thickness of $160 - 190 \mu m$), then baked and relaxed in the standard PAB step. It is exposed to a mercury lamp with a measured exposure dose of $1.3 J/cm^2$; the $365 nm$ Hg spectral line is well within the sensitivity range of the PAG. The films are hard-baked for $10 min$ at $62^\circ C$ until the film is completely polymerised. Whilst the coverslip is still on the hotplate, the IPA-saturated patterned structure is placed onto the adhesion layer and baked for several seconds (shown schematically in figure 3.10). As the solvent evaporates, surface tension flattens out the patterned film and causes it to stick to the adhesion layer. So long as the evaporation rate is low, the photonic crystal structure survives this procedure. The advantage of this method is that no further polymerisation of the photonic structure is possible.

When immersed in IPA and placed in an ultrasonic bath, the adhesion layer peels away

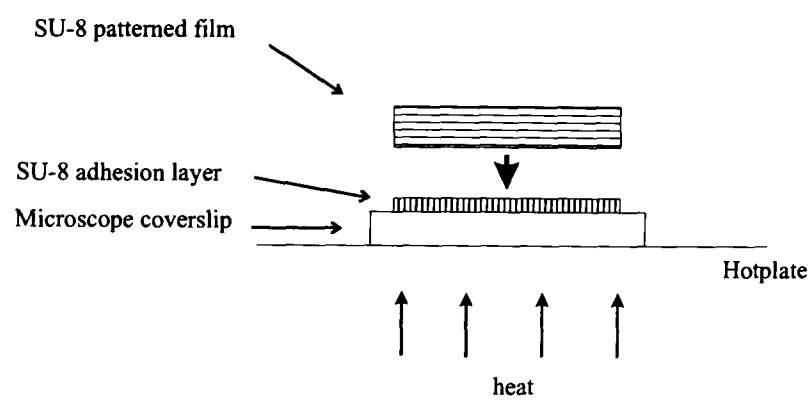


Figure 3.10: A thin film of fully polymerised SU-8 can act as an adhesion promoter for bonding patterned SU-8 films to silica surfaces. A fully developed, patterned film is baked to the polymerised adhesion layer; cross-links form at the interface.

from the substrate before the bonds between the patterned structure and the adhesion layer break. The bonds are stable, and several samples have survived for over a year at the time of writing. These observations indicate that cross-links most likely form between the film and the adhesion layer when baked, and it is these cross-links rather than simple surface tension forces that cause the photonic crystal to adhere to the adhesion layer.

This technique is not always reliable, and success currently depends on the user's experience. The length of time the structured film is heated on the adhesion layer and the evaporation rate of the solvent are critical, but the process has not yet been quantified. If the system is removed from the heat too soon, then although the patterned film will be much flatter than a normal air-dried film, cross-links do not form: as soon as the patterned film dries out, it lifts away from the adhesion layer. If the system is heated too long, the photonic crystal structure collapses, and the film loses its opalescence and turns white. The structure also collapses if the IPA evaporates too rapidly.

This method is not yet reliable enough for, and may never be suited to, industrial applications, but is adequate for producing flat films for optical transmission measurements

and for handling the samples.

3.6.2 SU-8 as an Adhesion Promoter: Failed Methodologies

Several techniques were investigated, which used SU-8 as the adhesion promoter, but combined exposure and adhesion of the patterned film. An SU-8 adhesion layer ($2-3\ \mu\text{m}$ thick) was spin-coated onto fused silica disks and then exposed to a mercury lamp. The adhesion layer was then hardbaked until the film was completely glassy, a sign of complete polymerisation. Microscope coverslips were not suitable in this instance since the disks were subsequently exposed to the laser interference pattern.

Two alternative procedures were then investigated. In the first case, the adhesion layer was re-exposed with the mercury lamp to activate any remaining PAG molecules, then spin-coated with the photonic crystal layer of photoresist. The photonic crystal was then prepared in the usual manner. The aim was to initiate cross-linkage between the adhesion and photonic crystal layers during the PAB before exposing the photonic crystal layer to the laser interference pattern. In the second case, the photonic crystal layer of photoresist was immediately spin-coated onto the adhesion layer, then prepared in the usual manner to see if, before exposing the photonic crystal layer, cross-linkage could be initiated by the continuation of the polymerisation chain-reaction in the adhesion layer or by diffusion of remnant protons into the photonic crystal layer.

A relatively thick adhesion layer of polymer has the advantage that the stresses due to polymerisation-induced shrinkage in the patterned film relax to some extent during development. However, the interface between the structured and the adhesion layers is unlikely to be well-defined since it is impossible to control the polymerisation chain reaction once initiated. In both the above cases, the photonic crystal layer partially

polymerised during the PAB. Polymerisation was initiated both by the diffusion of protons into the photonic crystal layer and by the continuation of the polymerisation chain reaction. When an acid-sensitive dye, rhodamine B, was incorporated into the photonic crystal photoresist, the dye changed colour during the PAB of the photonic crystal, indicating that remnant acid from the PAG diffused into the photonic crystal layer from the adhesion layer. In a separate experiment, the adhesion layer was rinsed with PGMEA to remove any residual activated PAG molecules before spin-coating the photonic crystal layer; the photonic crystal layer still partially polymerised. The polymerisation chain reaction propagated to a depth of $5\text{ }\mu\text{m}$ into the photonic crystal layer, making these films useless for exposure purposes.

Exposing the photonic crystals in the usual manner and then initiating cross-linkage to the adhesion layer after exposure, during the PEB step, instead of during the PAB step, before exposure, also resulted in overpolymerised structures.

3.6.3 Organosilanes as Adhesion Promoters

Organosilanes, compounds containing a silicon-carbon bond, are frequently used in industry as adhesion promoters or coupling agents for silica surfaces ([92] and references therein). Trifunctional silanes consist of a Si atom with a long, usually organic, bridging group and three alkoxy leaving groups attached to it. The silane can react up to three times with the silica surface via the alkoxy groups. Difunctional silanes, where one alkoxy group has been replaced with an inert methyl group, can only react twice with the silica surface. In both groups, the far end of the bridging group is attached to a functional organic group, which is tailored to the compound to be attached. In the case of SU-8, an epoxy-functional silane is used to coat the silica surface uniformly. In principle, the

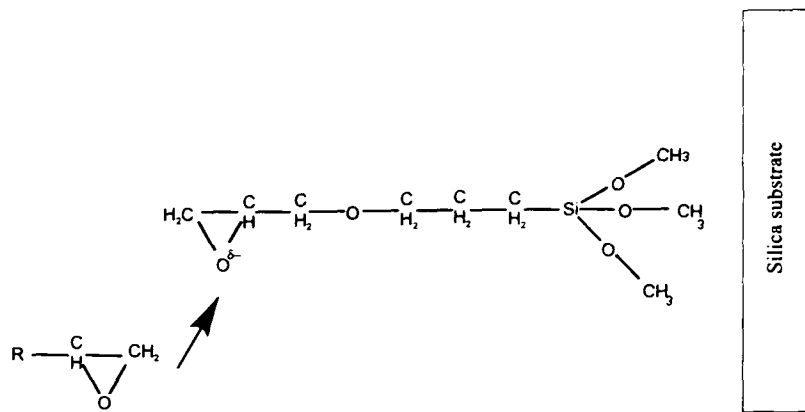


Figure 3.11: Glycidoxypentyl Tri-methoxy silane acts as an adhesion promoter between SU-8 and silica substrates. It can react with the silica surface up to three times via the alkoxy leaving groups, $\text{O} - \text{CH}_3$ and with SU-8 via the epoxy ring.

polymerisation chain reaction initiated in the patterned film during the PEB will then promote cross-linkage between the epoxy-groups of the silane and the SU-8.

The epoxy-functional silane, Glycidoxypentyl Tri-methoxy silane, was tried as an adhesion promoter between SU-8 and silica coverslips. The coverslips were silanised using a well-established recipe recommended by the suppliers of organosilanes, Gelest [92], and immediately spin-coated with SU-8. The photonic crystals were prepared in the standard manner. The photoresist did not wet the silanised surface very well. After the PAB, the spun film was very uneven, and the photoresist had retracted from the edges of the coverslip. Such films are not suitable for exposure since the surface unevenness leads to lensing during exposure, and the interference pattern is perturbed. Unfortunately, the films also detached from the coverslip during development, indicating that no cross-links formed between the silane and the SU-8 epoxy groups. We have not yet found a satisfactory explanation for this.

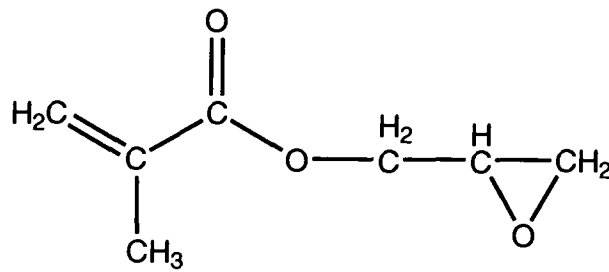


Figure 3.12: The carbon-carbon double bond of the Glycidyl Methacrylate molecule is selectively polymerised by a pulsed plasma whilst preserving the epoxy ring at the end of the organic chain. The epoxy ring is then available to react with SU-8 and serve as an adhesion promoter.

3.6.4 Pulsed Plasma Polymerisation of Glycidyl Methacrylate as an Adhesion Promoter

An alternative, solventless method for functionalising silica substrates with epoxy groups has been developed by Badyal and coworkers [93] and involves the pulsed plasma polymerisation of Glycidyl Methacrylate (shown in figure 3.12). In the right conditions, a pulsed plasma selectively polymerises the Methacrylate carbon-carbon double bond while preserving the epoxy ring at the end of the organic chain. A thin (5 – 20 *nm* thick) uniform layer of polymer is thus deposited on the substrate with intact epoxy groups at the film surface. The functionalised surfaces can then be used in adhesion promotion in the same way as the silanised substrates.

Functionalised silica substrates were supplied by the Badyal group. One set of substrates was immediately spin-coated with the standard photoresist. A second set of substrates was first soaked in a solution of 5% PAG in GBL with the aim of infiltrating the substrate coating with lots of initiation sites for cross-linking the photonic crystal to the adhesion layer. The photonic crystals were then prepared in the usual manner.

The photoresist coated the treated substrates extremely well, which we attribute to the lowering of the surface energy by functionalising the the substrates. Unfortunately, the photonic crystals became detached from the substrates during development, indicating that no cross-links formed between the patterned film and the adhesion layer. As before, we have no satisfactory explanation for this failure, though more recent work by Dr C. F. Blanford shows initial promise in promoting adhesion.

Chapter 4

922 *nm* Face-centred Cubic

Interference Pattern

In this chapter, I discuss the practical implementation of holographic lithography with reference to one particular structure, a face-centred cubic structure generated using an interference pattern which has an ideal conventional cube side of 922 *nm* in air with an interference wavelength of 355 *nm*. In section 4.1, I identify a chiral and non-chiral version of the 922 *nm* fcc interference pattern. In section 4.2, I review chiral photonic crystals and compare the bandstructures of non-chiral and chiral structures. In section 4.3, I describe how this interference pattern can be implemented to fabricate a face-centred cubic structure in SU-8. The resulting photonic crystal structures are then characterised by scanning electron microscopy (section 4.4).

4.1 Interference Patterns: Non-chiral and Chiral

The structures discussed in this chapter are all based on a face-centred cubic interference pattern with conventional cube side a and either a chiral or a non-chiral basis [78]. It is worth remembering at this point, as discussed in chapter 3.1, that the lattice geometry of the interference pattern is entirely determined by the laser wavevectors whereas the basis depends on the polarisation vectors and relative intensities of the four beams.

4.1.1 Wavevectors for the Face-centred Cubic Lattice

Four laser beams each point to a lattice site of the conventional unit cell of the reciprocal lattice; in this case, the conventional unit cell of the reciprocal lattice is a body-centred cubic (bcc) lattice with conventional cube side $4\pi/a$. The wavevectors of the four beams are the following:

$$\begin{aligned}
 \mathbf{k}_1 &= 2\pi/a [\bar{3}/2 \ \bar{3}/2 \ \bar{3}/2] \\
 \mathbf{k}_2 &= 2\pi/a [\bar{5}/2 \ \bar{1}/2 \ \bar{1}/2] \\
 \mathbf{k}_3 &= 2\pi/a [\bar{1}/2 \ \bar{5}/2 \ \bar{1}/2] \\
 \mathbf{k}_4 &= 2\pi/a [\bar{1}/2 \ \bar{1}/2 \ \bar{5}/2]
 \end{aligned} \tag{4.1}$$

with wavevector differences:

$$\begin{aligned}
 \Delta \mathbf{k}_{12} &= \mathbf{k}_1 - \mathbf{k}_2 = 2\pi/a [\bar{1}\bar{1}\bar{1}] \\
 \Delta \mathbf{k}_{13} &= \mathbf{k}_1 - \mathbf{k}_3 = 2\pi/a [\bar{1}\bar{1}\bar{1}] \\
 \Delta \mathbf{k}_{14} &= \mathbf{k}_1 - \mathbf{k}_4 = 2\pi/a [\bar{1}\bar{1}\bar{1}] \\
 \Delta \mathbf{k}_{23} &= \mathbf{k}_2 - \mathbf{k}_3 = 2\pi/a [\bar{2}20] \\
 \Delta \mathbf{k}_{24} &= \mathbf{k}_2 - \mathbf{k}_4 = 2\pi/a [\bar{2}02] \\
 \Delta \mathbf{k}_{34} &= \mathbf{k}_3 - \mathbf{k}_4 = 2\pi/a [0\bar{2}2]
 \end{aligned} \tag{4.2}$$

The wavevector differences thus generate a body-centred cubic reciprocal lattice, which corresponds to a real-space fcc lattice. This beam geometry, shown in figure 4.1, is highly symmetric: the central beam, $\mathbf{k}_1$, is vertically incident on the target, the three peripheral beams $\mathbf{k}_2$, $\mathbf{k}_3$ and $\mathbf{k}_4$ are each incident at an angle of 38.9° with respect to the vertical, each separated azimuthally by 120° . In air, this beam geometry generates an fcc lattice with a conventional cube side of $a = 3\sqrt{3}\lambda/2 = 922\text{ nm}$ for an interference wavelength of $\lambda = 355\text{ nm}$. The pattern is oriented so that the central beam lies along the $[111]$ direction.

4.1.2 Role of Polarisation Vectors and Relative Intensities in the Design of the Basis

The form of the basis can be controlled by placing constraints on the polarisation vectors and beam intensities. Threefold rotational symmetry along the $[111]$ axis is maintained by constraining the three peripheral beams to have the same intensities and rotationally symmetrical polarisation vectors. The central beam is circularly polarised, which ensures equal interference with each of the three peripheral beams. The peripheral beams are

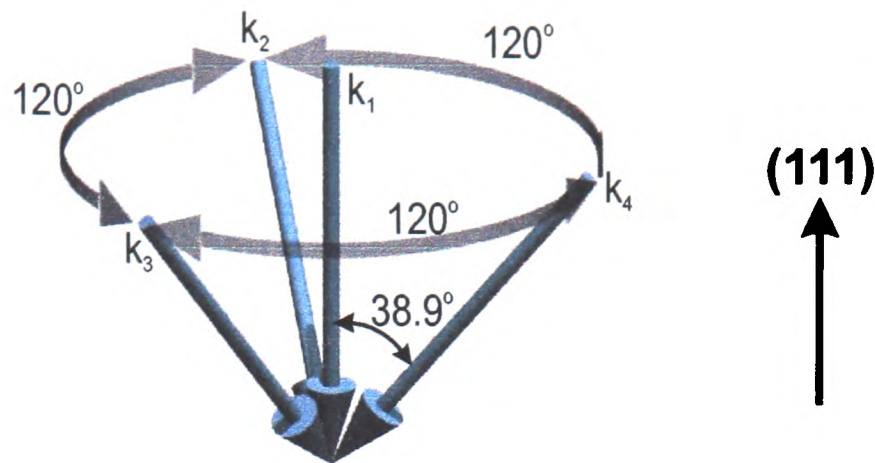


Figure 4.1: The beam geometry for the 922 nm face-centred cubic interference pattern is highly symmetric. The central beam is incident normally on the film surface, so that the (111) planes are parallel to the film surface.

linearly polarised. We measure the angle of polarisation with respect to the plane defined by the respective beam, $\mathbf{k}_i$, $i = 2, 3, 4$, and the central beam, $\mathbf{k}_1$. Thus, if the polarisation vector of a particular beam, $\mathbf{k}_2$ say, lies in the plane containing $\mathbf{k}_2$ and the central beam, $\mathbf{k}_1$, then the angle of polarisation is 0° . Positive angles are defined by the right-hand rule, so that looking in the direction of beam propagation, angles increase in the clockwise direction.

The interference patterns are orientated so that the (111) planes are parallel to the top surface. In this orientation, it is perhaps easier to visualise the fcc structure in terms of close-packed layers [10]; one period is made up of three layers a, b and c. The distance separating successive (111) planes in the interference pattern is equal to $a/\sqrt{3}$.

Figure 4.2 shows a calculated isosurface (surface of constant intensity), generated when the polarisation vectors of the three peripheral beams lie in the (111) plane (po-

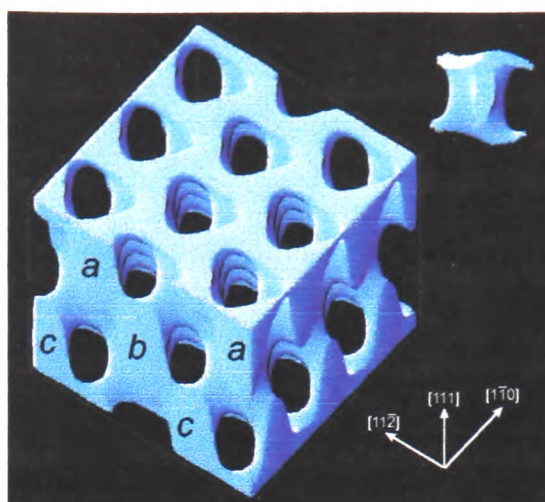


Figure 4.2: Isosurface of left-hand 922 nm fcc interference pattern with basis inset. The twist in the connecting arms is clearly visible. The close-packed layers are labelled a, b and c.

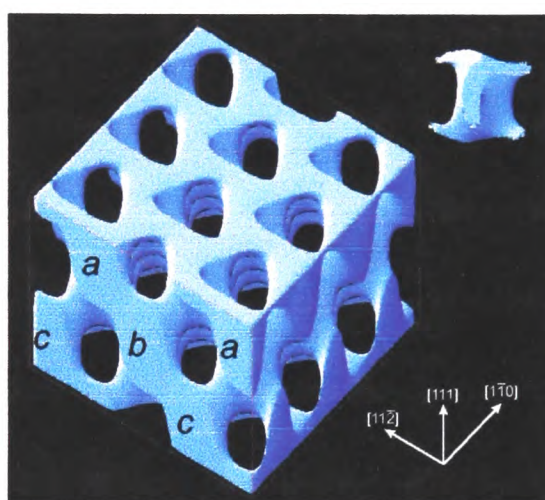


Figure 4.3: Isosurface of right-hand 922 nm fcc interference pattern with basis inset.

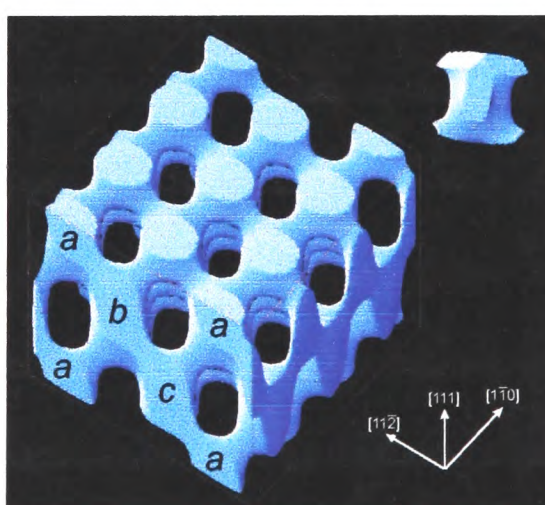


Figure 4.4: Isosurface of non-chiral 922 nm fcc interference pattern with basis inset. There is no inherent twist in the connecting arms of the basis.

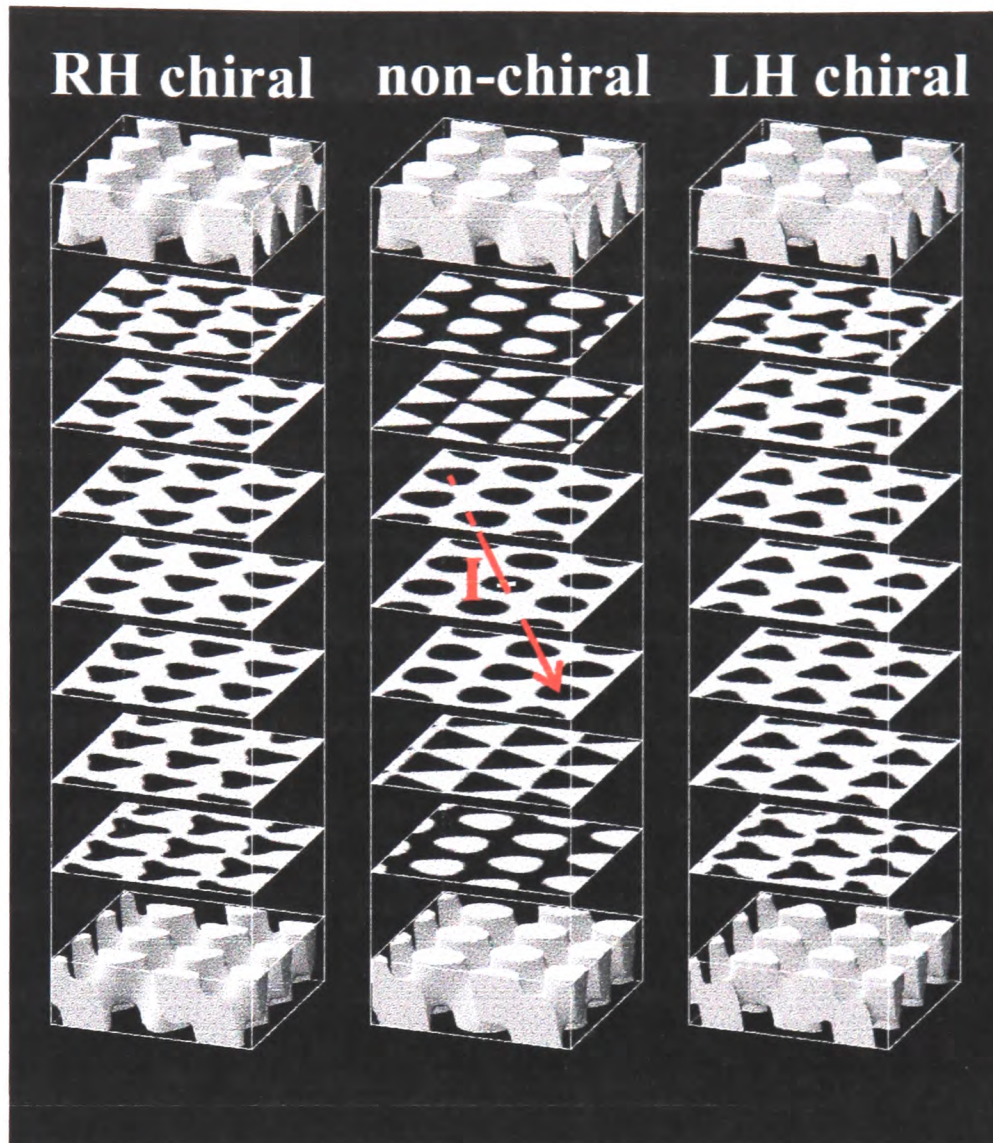


Figure 4.5: Exploded isosurfaces of right-hand chiral, non-chiral and left-hand chiral 922 nm fcc interference patterns show slices through the interference patterns parallel to the (111) planes between successive a and b close-packed layers. The voids are shown in black.

The non-chiral pattern has an inversion centre, which is absent in the case of the two chiral interference pattern. Some sections of the chiral patterns clearly show an inherent twist.

larisation angle 90°), and the central beam is left-hand circularly polarised. The same isosurface is shown in an ‘exploded’ version on the right-hand side of figure 4.5, which shows slices through the interference pattern parallel to the (111) planes between successive a and b close-packed layers. The voids in the isosurface are comparable to the ‘drilled holes’ of Yablonovite (c.f. figure 2.6).

Figure 4.3 shows the calculated isosurface, generated when the handedness of the circular polarisation in the central beam is changed to right-hand circular polarisation, and the peripheral beams are polarised in the (111) plane. An ‘exploded’ version of this isosurface is also shown on the left-hand side of figure 4.5.

Inset in figures 4.2 and 4.3 are the primitive basis for the two patterns. A twist in the ‘arms’ connecting the basis to their nearest neighbours is clearly visible. The handedness of the twist changes as the handedness of the circular polarisation in the central beam is changed. We therefore refer to these interference patterns as the left-hand and right-hand chiral patterns respectively. This inherent twist can clearly be seen in some sections of the ‘exploded’ isosurfaces of the chiral interference patterns.

From the IDL-generated isosurfaces, we calculate that the right- and left-hand interference patterns consist of a network of three-dimensionally interconnected voids and three-dimensionally interconnected material for volume fill fractions ranging from 21% to 85%. A network of three-dimensionally interconnected voids is an important practical attribute for film fabrication to ensure the unpolymerised material can be cleared out (c.f. section 3.5).

The basis is most obviously chiral when the peripheral beams are polarised in the (111) plane, at 90° . As the angles of polarisation are decreased simultaneously in the three peripheral beams, the twist in the ‘arms’ of the basis becomes less apparent. At a

polarisation angle of $\theta = \arccos\left(\frac{3}{4}\sqrt{\frac{3}{2}}\right) = 23.3^\circ$, the polarisation vectors of the peripheral beams are mutually orthogonal. The twist in the ‘arms’ connecting a basis to its nearest neighbours, shown inset in figure 4.4, has disappeared; we refer to this pattern as the non-chiral interference pattern.

The space group of the non-chiral pattern is $R\bar{3}m$. This pattern has an inversion centre, marked in red in figure 4.5. The non-chiral basis is mapped onto a non-chiral basis under a mirror operation, as shown in figure 4.6. There are three mirror planes in the non-chiral interference pattern, which are shown schematically in figure 4.7.

The chiral interference patterns belong to the lower symmetry space group $R32$. The mirror planes and inversion centre present in the non-chiral interference pattern are absent in the chiral patterns. Applying the mirror operation to the left-hand chiral interference pattern turns the left-hand chiral basis into the right-hand chiral basis and vice-versa, as shown in figure 4.8.

The cross-section of the cylindrical voids is circular at the midpoint between two successive close-packed planes of atoms; as figure 4.5 shows, the cross-section becomes triangular close to the planes of atoms, but there is no twist present in any sections. The non-chiral interference pattern has a network of interconnected void and material for a volume fill fraction ranging from 22% to 79%.

In the case of the non-chiral interference patterns, maximum intensity contrast is obtained when the intensities of the four beams are in the ratio 3:1:1:1, where the most intense beam is the central one, $\mathbf{k}_1$; in the case of the most chiral patterns, maximum intensity contrast is achieved when the intensities of the four beams are in the ratio 9:2:2:2, where the central beam is again the most intense [78].

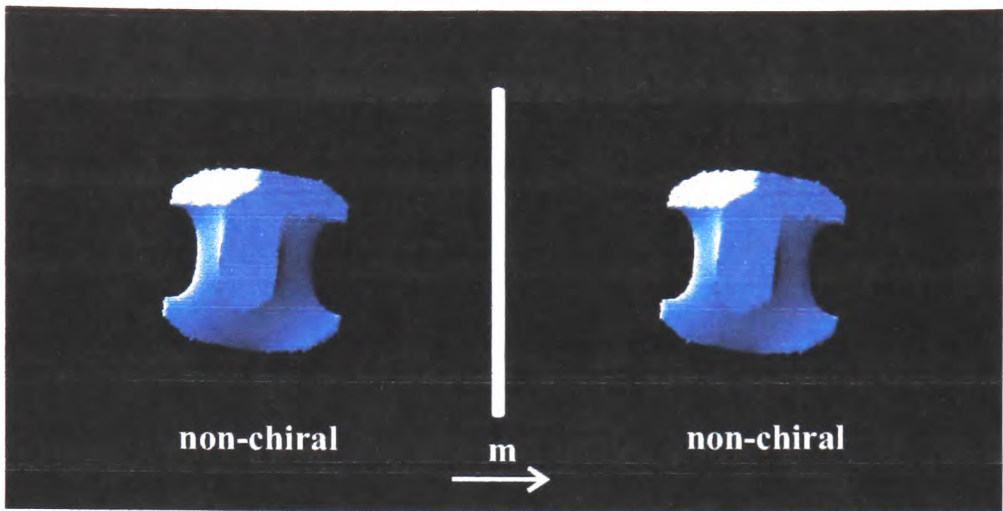


Figure 4.6: Under a mirror reflection, the non-chiral basis is mapped onto a non-chiral basis.

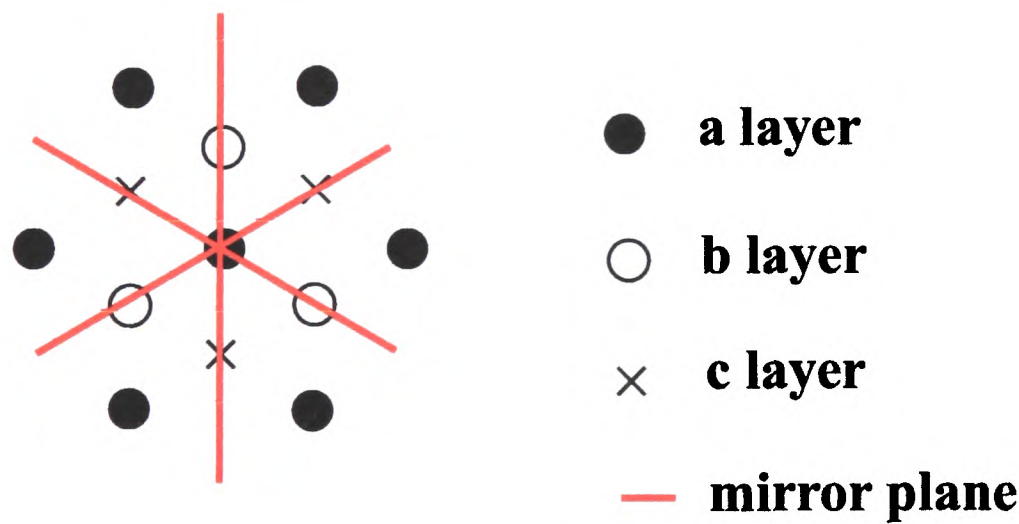


Figure 4.7: The three mirror planes in the non-chiral interference pattern are shown schematically. a, b and c mark the ‘atoms’ of the three close-packed layers.

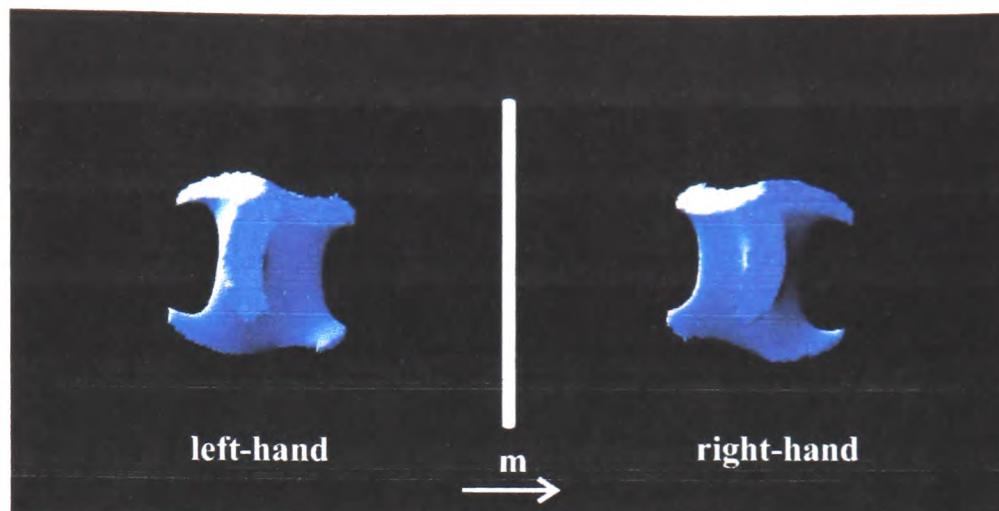


Figure 4.8: The mirror planes are absent in the chiral interference patterns as a mirror operation turns the left-hand basis into a right-hand basis and vice-versa.

4.1.3 Complete Photonic Bandgap in the Non-chiral Pattern?

Clearly, it is desirable that any structure produced with this interference pattern should have a complete, three-dimensional photonic bandgap.

I used the MIT Photonic-Bands code [14] to compute the photonic bandstructures of photonic crystals with air-filled voids, defined by these interference patterns. For a given interference pattern, there are two parameters which will influence the formation of photonic bandgaps in our structures, the fill fraction (ratio of material to void, determined by the threshold intensity of insolubility) and the refractive index contrast between material and void. A systematic search was made to identify the minimum fill-fraction and refractive index contrast required to open up a complete gap over the entire first Brillouin zone boundary.

In figure 4.9, I have plotted the photonic energy gap to mid-gap ratio as a function of fill-fraction at a number of refractive index contrasts for the non-chiral interference pattern. Each curve represents one refractive index contrast. The gap to mid-gap ratio is defined as the difference between the minimum energy of the third band, $\min(\omega_3)$, and

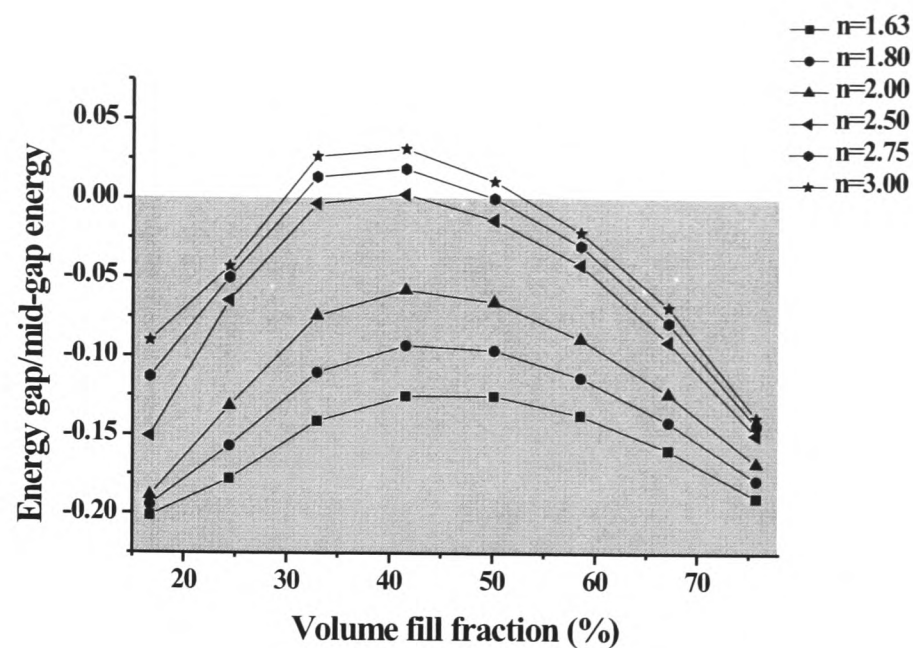


Figure 4.9: The photonic energy gap to mid-gap ratio for the second and third photonic bands is plotted as a function of volume fill fraction for the non-chiral interference pattern. Each curve represents a single refractive index contrast. A positive gap to mid-gap ratio implies that a complete three-dimensional photonic bandgap has opened up; a negative ratio implies that the energy gap between the second and third bands does not overlap in all directions in reciprocal space. A complete band gap first opens up for the non-chiral structure for a refractive index contrast of 2.50 and a fill fraction of 42% material to void.

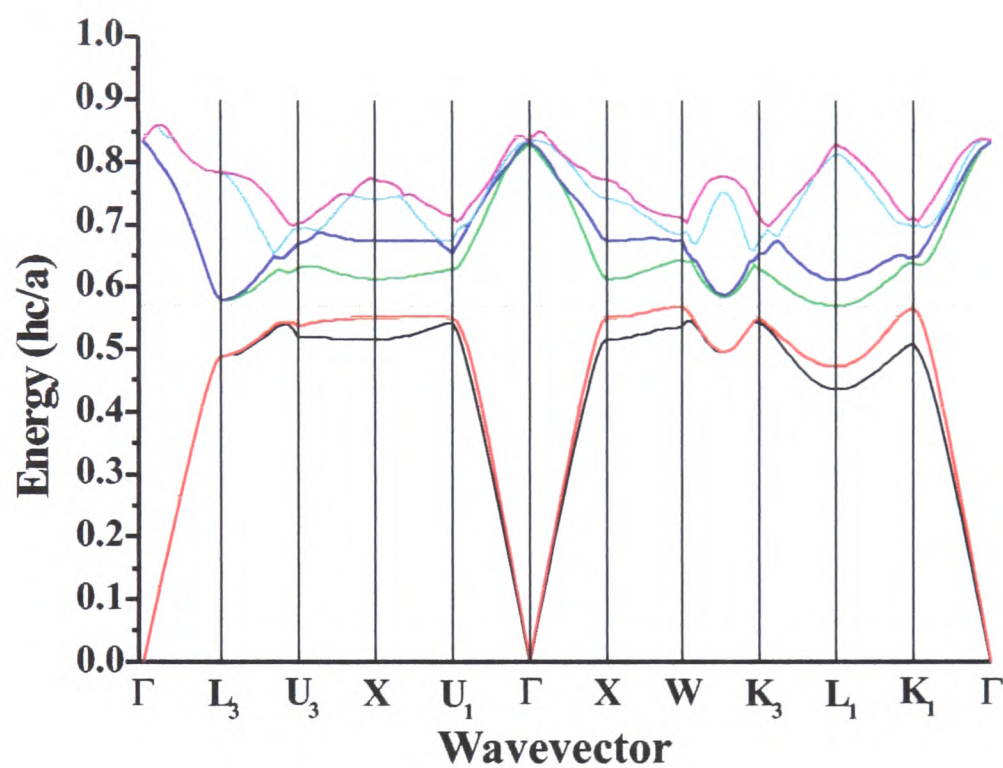


Figure 4.10: The photonic bandstructure is plotted for a non-chiral interference pattern with a refractive index contrast of 2.50 and a volume fill fraction of 42% material to void. These are the parameters for which a complete photonic bandgap, shaded in grey, first opens up between the second and third bands.

the maximum energy of the second band, $\max(\omega_2)$, divided by the mid-gap energy:

$$r_{\text{gap/mid-gap}} = 2 \frac{\min(\omega_3) - \max(\omega_2)}{\min(\omega_3) + \max(\omega_2)} \quad (4.3)$$

A positive ratio implies that a complete energy gap has opened up in all directions of reciprocal space; a negative ratio that a complete energy gap does not exist as the energy gaps in different directions of reciprocal space do not all overlap in energy. Figure 4.9 shows that a complete energy gap first opens up between the second and third band for a refractive index contrast of $n = 2.50$ at a fill fraction of 42% material to void in the non-chiral interference pattern. Figure 4.10 shows the bandstructure with the complete gap between the second and third bands for such a photonic crystal.

In practice, a structure with a volume fill fraction of 42% would have full three-dimensional connectivity, but it would be very fragile. Furthermore, it is clearly not possible to fabricate a structure with a complete photonic bandgap in SU-8 as the refractive index of SU-8 is too low ($n_{\text{SU-8}} = 1.63$). Achieving a refractive index contrast of 2.50 will require templating the original structure, then infilling the inverse structure again with some higher index material such as titania (TiO_2 in the rutile crystal form with a refractive index of ~ 2.8 [52]). The bandgap between the second and third band is the fundamental gap; we expect it to be less fragile to nonuniformity in the structures than, say, the bandgap which opens up between the eighth and ninth band in inverse-opals [79].

Although no complete bandgap can open up in an SU-8 photonic crystal exposed to the non-chiral interference pattern, figure 4.11 shows that the first transmission gap in the $\Gamma - \text{L}_3$ direction occurs at an energy of 0.633, which corresponds to a wavelength of $566/0.633 \approx 900 \text{ nm}$ for a lattice constant of $922/1.63 = 566 \text{ nm}$ and a volume fill fraction of 59% material to void. The gap energy increases with increasing fill fraction.

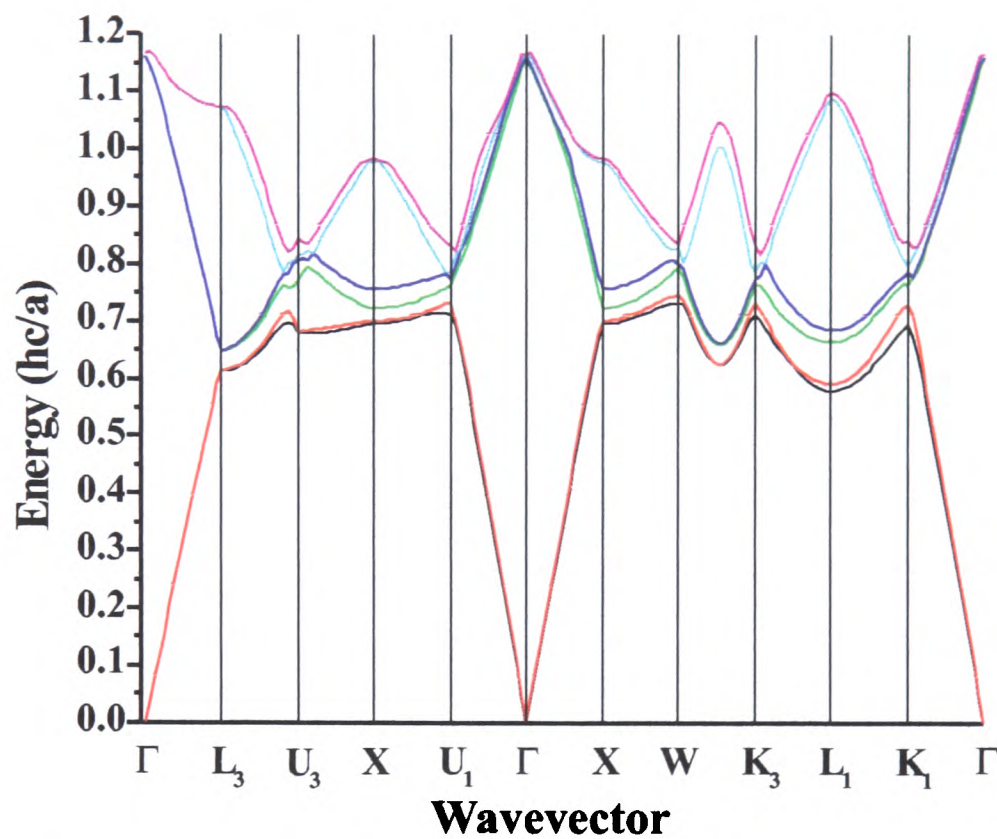


Figure 4.11: The photonic bandstructure is plotted for a non-chiral interference pattern with the refractive index contrast of SU-8 (1.63) and a volume fill fraction of 59% material to void. No complete photonic bandgap can open up at this refractive index contrast. The first transmission gap along the $[111]$ axis occurs at an energy of 0.633 ($566/0.633 = 895\text{ nm}$ for an ideal lattice constant in SU-8 of $922/1.63 = 566\text{ nm}$).

4.2 Chiral Interference Patterns

In the previous section, I showed that we could generate both chiral and non-chiral interference patterns. It is known that the geometry of the basis can have a significant effect on the photonic bandstructure for a fixed lattice type. Furthermore, spiral structures have been shown to produce photonic crystals with large photonic bandgaps [94]. The authors conclude that the structure of the basis is very important in the formation of the bandgap and that a basis consisting of a spiral rod favours the opening up of a bandgap. Given that our structures can be thought of as spiral-shaped air rods in a dielectric background (as shown in figure 4.5), I would like to investigate what, if any, effect the structure of the basis has on bandgap formation by examining the parameters required to open up a bandgap in a right-hand chiral structure.

In figure 4.12, I have plotted the photonic energy gap to mid-gap ratio between the second and third bands as a function of volume fill fraction and refractive index contrast for a right-hand chiral interference pattern. Each curve represents a single refractive index contrast value. The interference pattern was generated with the linear polarisation angles in the peripheral beams set at 90° , which is the condition required for the most chiral basis. As described in section 4.1.3, a positive gap to mid-gap ratio implies that a complete bandgap has opened up; a negative one that there is no full three-dimensional bandgap between the second and third bands.

The figure shows that the gap to mid-gap ratio is always negative for a refractive index contrast of 2.50, implying that a full three-dimensional photonic bandgap does not form at this refractive index contrast. In the case of the non-chiral pattern, a full bandgap forms at a refractive index contrast of 2.50 and a fill fraction of 42%; in the right-handed pattern, a full bandgap does not open up until the refractive index contrast

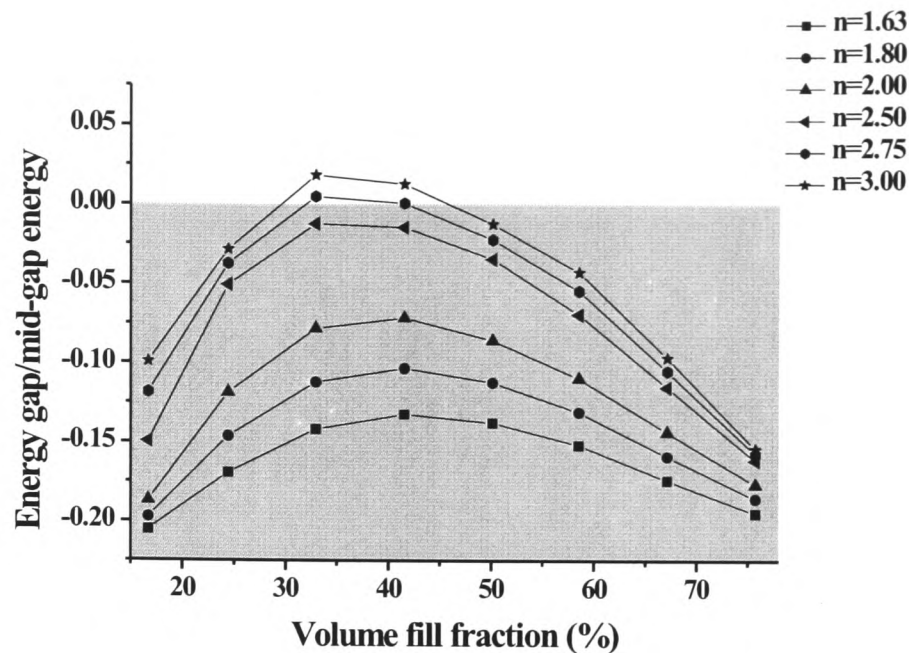


Figure 4.12: The energy gap to mid-gap ratio between the second and third photonic bands is plotted as a function of volume fill fraction for a right-hand chiral structure, generated with peripheral linear polarisation vectors set at 90° . Each curve represents one refractive index contrast between material and void. A positive ratio indicates that a complete photonic bandgap has opened up in all directions; a full three-dimensional photonic bandgap first opens up for a fill fraction of 42% material to void and a refractive index contrast of ≈ 2.75 . Comparing with figure 4.9, it becomes clear that the refractive index contrast required to open up a complete bandgap in the right-hand chiral structure is higher than in the non-chiral structure; the non-chiral basis is marginally more favourable to the formation of a complete bandgap.

reaches ≈ 2.75 . For the same fixed parameters, the bandgap in the non-chiral pattern is typically larger than that of the chiral pattern. It is possible to find parameters where this trend reverses, for example when the refractive index contrast is 3.00 and the fill fraction 24.4%. In general however, we can conclude that the non-chiral basis favours the formation of full photonic bandgaps in our structures.

4.3 Implementation of the Face-centred Cubic Structure

In practice, how do we adjust the beam geometry to produce a face-centred cubic interference pattern inside the photoresist? If a film of SU-8 is exposed directly to the wavevectors given by equation 4.1, then refraction at the air-resist interface will stretch the lattice of the interference pattern along the [111] direction as reported by Sharp [78].

The central beam, $\mathbf{k}_1$, is incident normally to the film surface, so the wavevector is not refracted, as shown in figure 4.13. The three peripheral beams however are refracted at the air-film surface. To generate a face-centred cubic interference pattern inside the resist, the internal angle of the three peripheral beams with respect to the vertical or [111] has to be $\theta_2 = 38.9^\circ$, as described in equations 4.1. Snell's law then determines the external, unrefracted angle, θ_1 , with respect to the vertical direction:

$$\theta_1 = \arcsin(n \sin\theta_2) = \arcsin(\underbrace{1.63 \sin 38.9^\circ}_{>1}) \quad (4.4)$$

where n is the refractive index of SU-8. θ_2 is greater than the critical angle in SU-8: it is therefore impossible to refract the external wavevectors directly to form a refracted face-centred cubic interference pattern inside the resist.

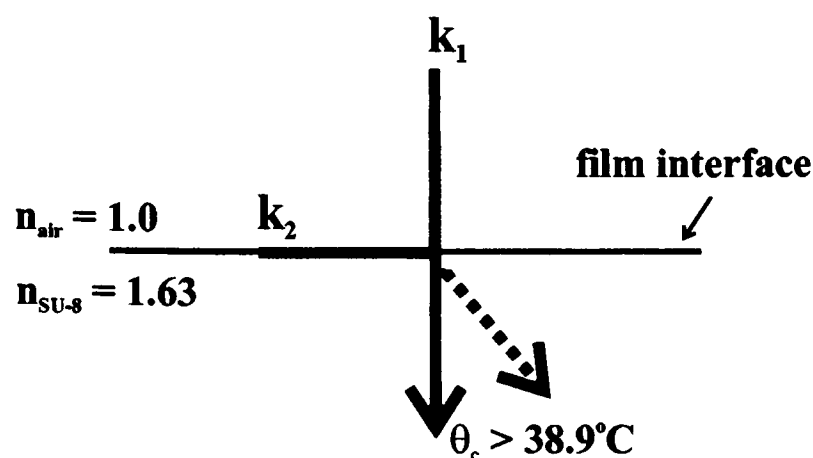


Figure 4.13: If the interference pattern is refracted directly from air into the SU-8 photoresist, the interference pattern is stretched along [111]. In this arrangement it is impossible to adjust the angles of the beams to generate an fcc lattice in SU-8, as the required peripheral beam angle is larger than the critical angle of SU-8.

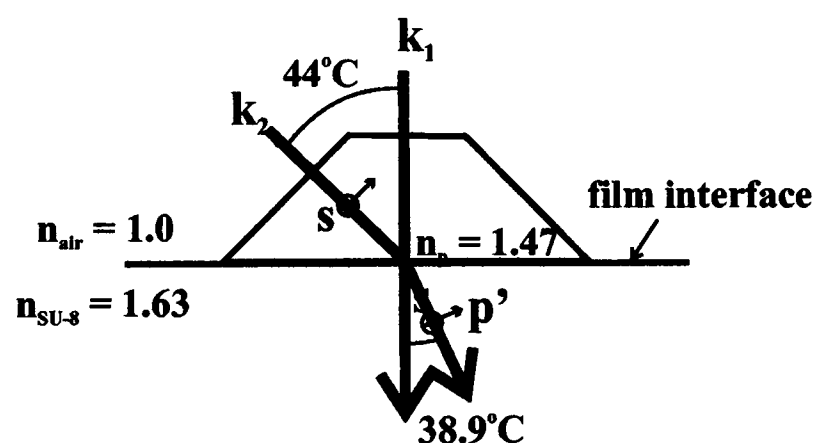


Figure 4.14: This holographic beam geometry generates an fcc lattice inside a film of SU-8 ($n = 1.63$). The four laser beams are refracted through a specially designed, truncated equilateral prism, made of fused silica ($n = 1.47$), which is approximately index-matched to the SU-8.

If the beams are refracted through a suitably designed prism, then it is possible to generate a face-centred cubic structure. The specially commissioned prism is a truncated equilateral triangle; the prism sides form an angle of 45° with respect to the vertical. It is made of UV-grade fused silica with a refractive index of 1.47 at the exposure wavelength of 355 nm. The facets of the prism have been polished to a surface flatness of $\lambda/4$. We use spectroscopic grade mineral oil with a refractive index of $n = 1.47$ as an index-matching medium at the prism-resist interface to allow coupling of the wavevectors into the resist. Spectroscopic grade ensures a high purity oil thus reducing the number of scatterers, which would perturb the interference pattern.

The external wavevector angles required to generate a face-centred cubic interference pattern inside the resist can be calculated using Snell's law. The ray diagram of the optical set-up is shown in figure 4.14. The central beam, k_0 , incident normally on the truncated surface of the prism, is not deviated at either the air-prism or the prism-resist interface. Only the three peripheral beams are refracted. At the prism-resist interface, the angle of incidence is given by:

$$\phi_1 = \arcsin\left(\frac{n_2}{n_1} \sin\phi_2\right) \quad (4.5)$$

where ϕ_1 is the peripheral wavevector angle incident on the prism-resist interface, ϕ_2 the refracted wavevector angle, $n_1 = 1.47$ the refractive index inside the prism and $n_2 = 1.63$ the refractive index inside the resist at the exposure wavelength of 355 nm. Similarly, the angle of incidence at the air-prism interface is given by:

$$\theta_0 = \arcsin(n_1 \sin\theta_1) \quad (4.6)$$

where θ_0 is the peripheral wavevector angle incident on the air-prism interface, $\theta_1 = 45^\circ - \phi_1$ the refracted wavevector angle and $n_1 = 1.47$ the refractive index inside the prism at 355 nm.

The peripheral wavevectors' angle incident on the prism facet can then be calculated:

$$\theta_0 = \arcsin(n_1 \sin\theta_1) = 1.3^\circ \quad (4.7)$$

The three peripheral beams therefore need to be at an external angle of $45^\circ - 1.3^\circ \approx 44^\circ$ with respect to the vertical axis.

The beams are aligned through the prism using a target marked with a cross and aligning each beam in turn on the cross. An additional benefit of the prism is that it reduces the angle of misalignment of the interference pattern with respect to the film surface. When $\mathbf{k}_1$ 'fills' the top facet of the prism, the angle of acceptance over which the beam both passes through the truncated surface of the prism and is centred on the target is greatly reduced.

It is important to ensure that the beams do not overfill the prism facets and refract into the prism through multiple facets. A structure exposed to an interference pattern of five beams as a result of this problem is shown in figure 4.15. This structure is generated when a peripheral beam overfills the prism facet and is refracted into the film through both the side and the top prism facets. We can calculate the ratio of the refracted wavevector difference to the refracted peripheral wavevector in the (111) plane:

$$\frac{\Delta \mathbf{k}_{\parallel}}{\mathbf{k}_{1\parallel}} = \frac{\sin(39^\circ) - \sin(29^\circ)}{\sin(39^\circ)} = \frac{1}{3} \quad (4.8)$$

which is in agreement with the observation that every third row of 'atoms' in the (111) surface is overexposed.

The effect of the prism on the polarisations also needs to be considered.

The transmission coefficients for s and p-polarisation are the following [95]:

$$t_s = \frac{2n_i \cos(\theta_i)}{n_i \cos(\theta_i) + n_t \cos(\theta_t)} \quad (4.9)$$

$$t_p = \frac{2n_i \cos(\theta_i)}{n_t \cos(\theta_i) + n_i \cos(\theta_t)} \quad (4.10)$$

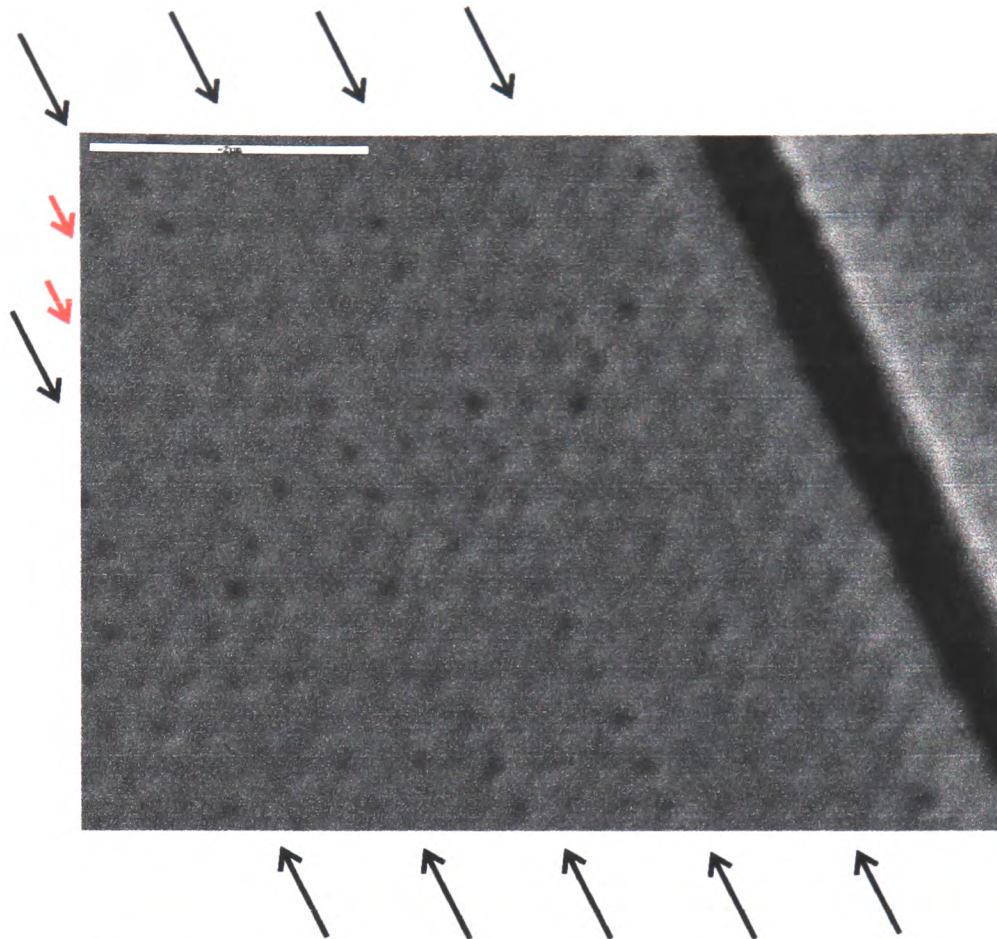


Figure 4.15: Scanning electron micrograph of a structure exposed to a five-beam interference pattern as a result of the peripheral beams overfilling the prism facets. As a result, the structure consists of a one-dimensional grating, marked with black arrows, superimposed on the ordinary lattice, marked with red arrows. This pattern arises when a peripheral beam overfills the facet of the prism and is refracted into the film through both the side and the top prism facets. The ratio of the refracted wavevector difference to the refracted peripheral beam in the (111) plane is $1/3$, which is in agreement with the observation that every third row of atoms is overexposed.

where the subscripts s and p refer to s, respectively p-polarisation, the subscripts i and t refer to the incident, respectively transmission medium, n is the refractive index, θ_i the angle of incidence and θ_t the angle of refraction.

The central, circularly polarised beam is normally incident on the top facet of the prism. Hence, s and p polarisation states are not strictly defined, and the transmission coefficients for normal incidence are simply:

$$\begin{aligned} t_{air-prism} &= \frac{2n_i}{n_i + n_t} = \frac{2}{1 + 1.47} = 81.0\% \\ t_{prism-film} &= \frac{2n_i}{n_i + n_t} = \frac{2 \cdot 1.47}{1.47 + 1.63} = 94.8\% \end{aligned} \quad (4.11)$$

The polarisation state of the central beam is hence not affected by refraction; the absolute intensity in the central beam can be adjusted to take account of reflection losses.

The three peripheral beams are incident at an angle of approximately 1° with respect to the facet normal at the air-prism interface (c.f. equation 4.7) and at an angle of $\theta_1 = \arcsin(\frac{n_2}{n_1} \sin(38.9^\circ)) = 44^\circ$ at the prism-film interface. Assuming normal incidence at the air-prism interface, the transmission coefficient is 81%; the transmission coefficients at the prism-film interface are:

$$t_s = \frac{2 \cdot 1.47 \cos(44^\circ)}{1.47 \cos(44^\circ) + 1.63 \cos(38.9^\circ)} = 90.9\% \quad (4.12)$$

$$t_p = \frac{2 \cdot 1.47 \cos(44^\circ)}{1.63 \cos(44^\circ) + 1.47 \cos(38.9^\circ)} = 86.6\% \quad (4.13)$$

In the first instance, we must note that the transmission coefficients for s and p-polarisations are no longer the same, which implies that the polarisation vector rotates as it passes through the prism. Let us calculate whether this rotation is significant.

Consider the wavevector of the peripheral beam $\mathbf{k}_2$. Using an orthonormal basis ($\mathbf{s}$, $\mathbf{p}$), attached to the unrefracted beam at the prism-film interface, as shown in figure 4.14, the

polarisation vector of the beam incident on the prism-film interface can be written as:

$$\begin{aligned}\mathbf{u}_i &= \alpha \mathbf{s} + \beta \mathbf{p}, & 0 \leq \alpha \leq 1 \\ & & 0 \leq \beta \leq 1\end{aligned}\tag{4.14}$$

where α and β are the coordinates of the polarisation vector. Note that for the purposes of this calculation, the polarisation vectors $\mathbf{u}$ are not normalised.

Using an orthonormal basis $(\mathbf{s}, \mathbf{p}')$ attached to the refracted beam, the polarisation vector of the refracted beam can be written as:

$$\mathbf{u}_r = t_s \alpha \mathbf{s} + t_p \beta \mathbf{p} \tag{4.15}$$

where the factors t_s and t_p are the transmission coefficients calculated in equations 4.12 and 4.13.

We want to calculate how much the polarisation vector rotates across the prism-resist interface. The angle between the polarisation vectors of the incident and refracted beams can be calculated as follows:

$$\begin{aligned}\cos\theta(\alpha, \beta) &= \frac{\mathbf{u}_i \cdot \mathbf{u}_r}{|\mathbf{u}_i| \cdot |\mathbf{u}_r|} \\ &= \frac{t_s \alpha^2 + t_p \beta^2}{\sqrt{(\alpha^2 + \beta^2)(t_s^2 \alpha^2 + t_p^2 \beta^2)}}\end{aligned}\tag{4.16}$$

Therefore:

$$\theta(\alpha, \beta) = \arccos\left(\frac{t_s \alpha^2 + t_p \beta^2}{\sqrt{(\alpha^2 + \beta^2)(t_s^2 \alpha^2 + t_p^2 \beta^2)}}\right)\tag{4.17}$$

In order to determine the maximum angle of rotation, we need to consider the partial

derivatives of θ with respect to α and β .

$$\begin{aligned} \left(\frac{\partial\theta}{\partial\alpha}\right)_\beta &= \frac{-1}{\sqrt{1 - \frac{(t_s\alpha^2 + t_p\beta^2)^2}{(\alpha^2 + \beta^2)(t_s^2\alpha^2 + t_p^2\beta^2)}}} \\ &\cdot \left\{ -\frac{\alpha(t_s\alpha^2 + t_p\beta^2)[2 \cdot t_s^2\alpha^2 + (t_p^2 + t_s^2)\beta^2]}{(\alpha^2 + \beta^2)^{3/2}(t_s^2\alpha^2 + t_p^2\beta^2)^{3/2}} \right. \\ &\left. + \frac{2 \cdot t_s\alpha(\alpha^2 + \beta^2)(t_s^2\alpha^2 + t_p^2\beta^2)}{(\alpha^2 + \beta^2)^{3/2}(t_s^2\alpha^2 + t_p^2\beta^2)^{3/2}} \right\} \end{aligned} \quad (4.18)$$

The partial derivative is set to 0 to find the maxima and minima. Some rearranging gives the following result:

$$\left(\frac{\partial\theta}{\partial\alpha}\right)_\beta = 0 \Leftrightarrow \alpha = 0 \quad \text{or} \quad \beta = 0 \quad \text{or} \quad \alpha^2 = \frac{t_p}{t_s}\beta^2 \quad (4.19)$$

Substituting in equation 4.17, we find that the maximum angle through which the polarisation vector of the peripheral beam will be rotated is:

$$\theta_{max} = 1.4^\circ \quad (4.20)$$

If we repeat the above calculation for the partial derivative with respect to β , we will get the same angle. Given that the graduation on the rotation stages in which the polarising cubes are mounted is only 2° , we can safely ignore any rotation of the polarisation vectors due to the prism.

The relative intensities in the peripheral beams can be adjusted to take account of any energy losses due to reflections at the interfaces.

4.4 Characterisation of the Photonic Crystals by Scanning Electron Microscopy

Scanning electron micrographs show that photonic crystals fabricated by holographic lithography are generally defect-free over hundreds of unit cells. Figure 4.16 shows a

scanning electron micrograph of either the top or bottom surface, a (111) plane, of a structure exposed to a non-chiral face-centred cubic interference pattern with a lattice constant of 922 nm in air. No twist is visible in the ‘arms’ connecting nearest-neighbour basis, which indicates that the basis is non-chiral.

Figure 4.17 shows a close-up scanning electron micrograph of a top or bottom surface of a structure exposed to the non-chiral fcc pattern, and figure 4.18 is a fast Fourier transform (FFT) of figure 4.17. The FFT shows the characteristic six first order diffraction spots of a hexagonal structure. The structure is not quite regular. The nearest-neighbour spacing in the (111) plane of the interference pattern inside the resist is $a/\sqrt{2}/n = 922/\sqrt{2}/1.63 = 400 \text{ nm}$; nearest-neighbour spacing in the (111) plane of the polymerised structures, estimated from figure 4.18, is 360 nm. In-plane shrinkage during fabrication is therefore $40/400 = 10\%$.

Figure 4.19 shows a scanning electron micrograph of a ($\bar{1}11$) cleavage plane of a structure exposed to the 922 nm left-hand chiral face-centred cubic pattern (SEM conditions are identical to those in figure 4.16). Figure 4.20 is a close-up of the basis, which shows the characteristic ‘twist’ in the arms of the chiral basis. The integrity of the structure is maintained over ~ 45 planes. (111) plane spacing in the interference pattern inside the resist is $a/\sqrt{3}/n = 922/\sqrt{3}/1.63 = 327 \text{ nm}$; the plane spacing in the polymerised structures, estimated from figure 4.19, is 260 nm. Note that this is a rough estimate as the sample was not aligned with the (111) planes parallel to the electron beam in figure 4.19. Furthermore, the cleavage plane is not normal to the (111) plane. Estimated shrinkage between (111) planes is therefore $67/327 = 20\%$.

When the films are misaligned with respect to the interference pattern, banding appears on the micrographs. The bands correspond to regions where the film surface cuts

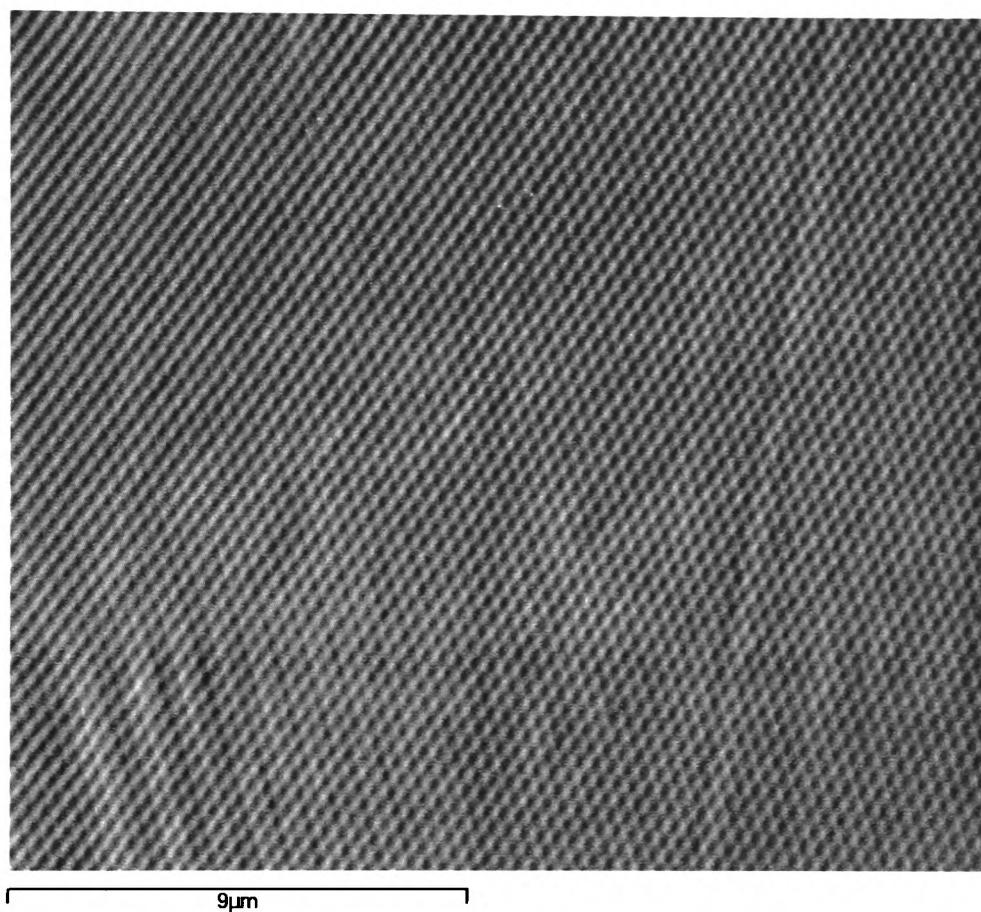


Figure 4.16: The scanning electron micrograph of the surface (a (111) plane) of a structure exposed to the 922 nm non-chiral face-centred cubic interference pattern shows that the structures are defect-free over hundreds of unit cells.

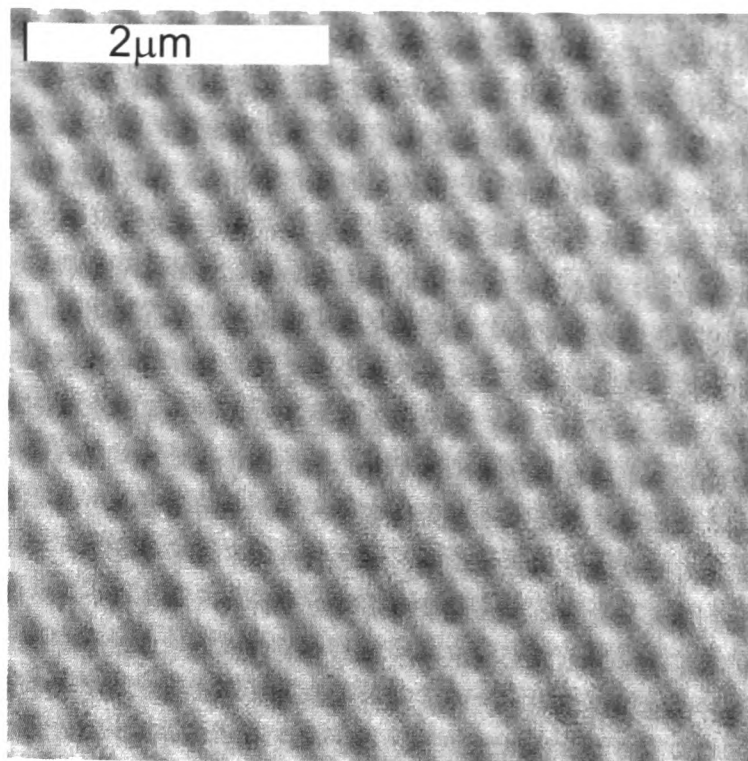


Figure 4.17: The scanning electron micrograph shows a section of (111) plane of a structure exposed to the 922 nm non-chiral face-centred cubic interference pattern.

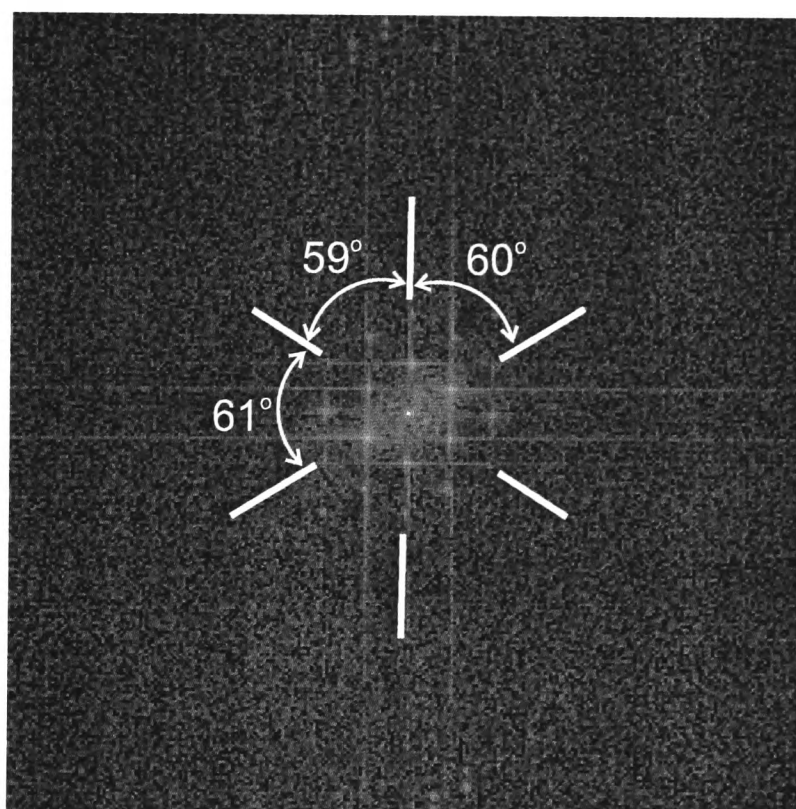


Figure 4.18: The Fourier Transform of the above SEM image shows the characteristic six first order diffraction spots, which are indicative of a hexagonal array. Some second order features are also visible.

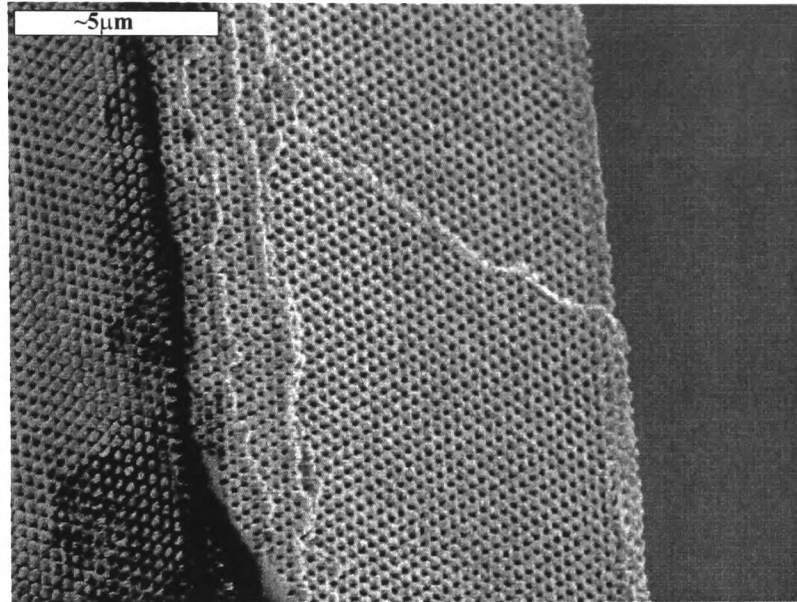


Figure 4.19: The scanning electron micrograph shows a $(\bar{1}11)$ cleavage plane of a structure exposed to the 922 nm left-hand chiral face-centred cubic interference pattern.

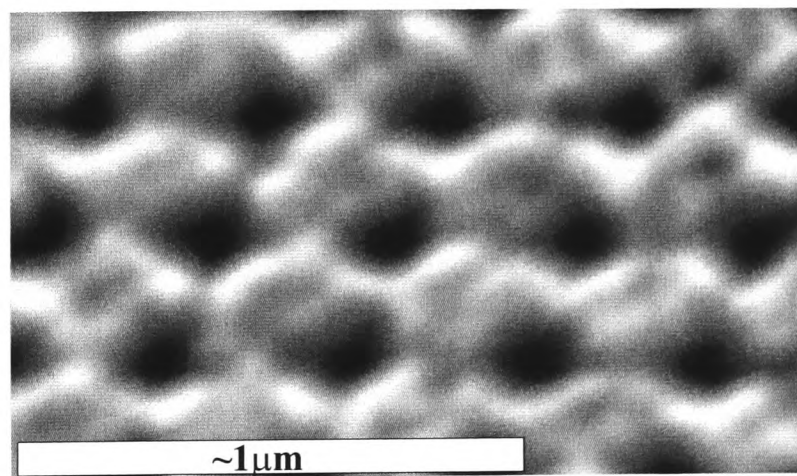


Figure 4.20: The scanning electron micrograph shows the left-hand chiral basis in a $(\bar{1}11)$ cleavage plane.

through the close-packed layers in the interference pattern. Consequently, an image of a film surface can contain depth information about the interference pattern, and can be pictured as a series of cross-sections through the unit cell taken at slightly different heights. By stacking these cross-sections, it is possible to produce a three-dimensional reconstruction of the crystal [78].

Figures 4.4 and 4.4 show scanning electron micrographs of the top surfaces of a left-hand, a right-hand chiral and a non-chiral photonic crystal, where the interference pattern has been deliberately misaligned by 3° with respect to all three film surfaces. The chiral structures have been produced using the most chiral interference patterns (the peripheral polarisation vectors set at 90°). The bands marked a and b are regions where the film surface cuts through successive close-packed layers of the interference pattern.

The voids in the chiral structures in figure 4.4 have triangular cross-sections whereas the cross-section of the voids in the non-chiral structure in figure 4.4 is circular at the midpoint between the bands, but becomes triangular closer to the edges of the close-packed layers. The successive voids along the direction normal to the direction of the bands are in effect equivalent to cross-sections of the air cylinder taken at different heights as the cylinder passes from the (111) plane a to the (111) plane b. The micrograph of the non-chiral structure has an inversion centre, as we would expect from the interference patterns described in section 4.1.

In the chiral micrographs in figure 4.4, one side of the triangular void has been marked with an arrow. Following the successive voids along the direction normal to the direction of the band as indicated in the figure, we see that the triangles rotate and that the direction of rotation changes with the handedness of the basis. Furthermore, the triangles rotate by 120° between two successive (111) planes. So the chiral period, i.e.

the length scale over which the triangle completes a full rotation, is equal to the cube diagonal of the face-centred cubic interference pattern.

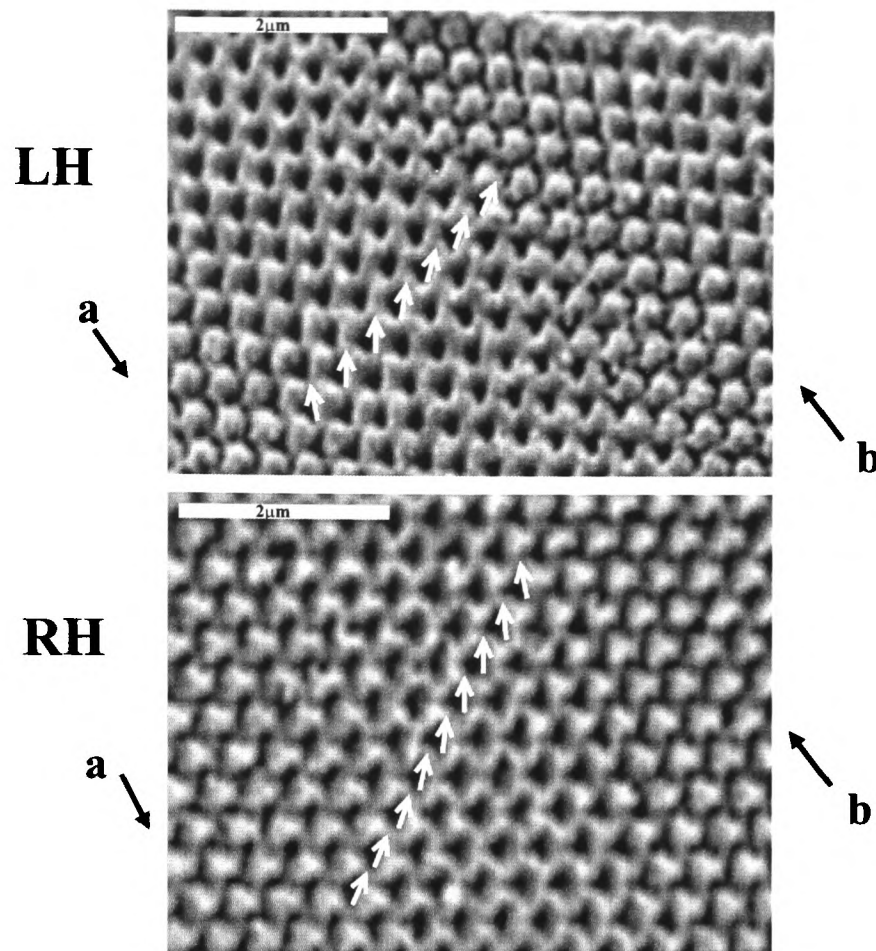


Figure 4.21: The top, respective bottom, SEM images show the top surface of a left-hand, respective right-hand, chiral structure. The bands where the crystal surface cuts through successive close-packed layers of the interference pattern are marked a and b. The inherent twist in the ‘arms’ of the chiral basis connecting nearest neighbours is particularly clear in the region between close-packed layers. Alternatively, we can analyse the ‘voids’. One side of the triangular voids has been marked with an arrow. Following successive voids along the direction normal to the direction of the band is equivalent to following an air cylinder from one close-packed layer down to the following layer. The triangular voids rotate as we ‘pass down through’ the crystal; the direction of rotation changes with the handedness of the basis.

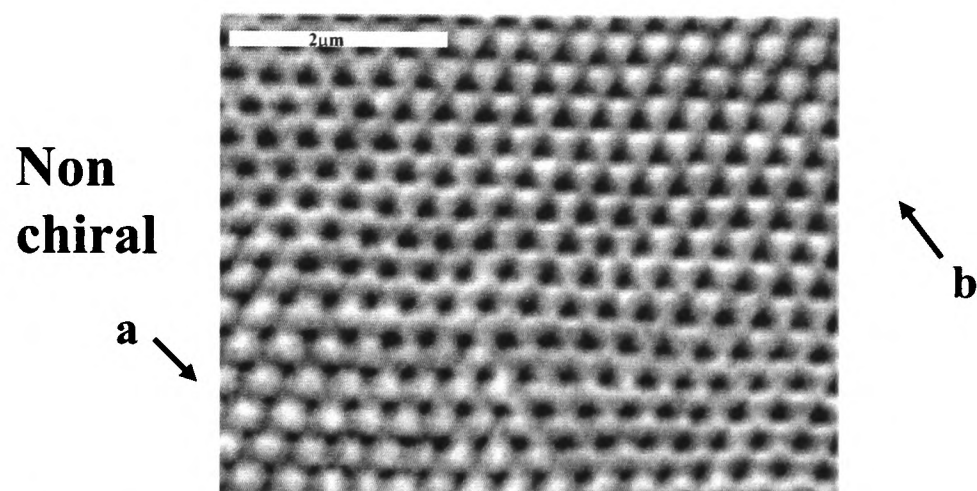


Figure 4.22: The SEM image shows the top surface of a photonic crystal exposed to a face-centred cubic interference pattern with a non-chiral basis.

Chapter 5

Optical Characterisation of the Photonic Crystals

The dried polymer-air face-centred cubic crystals strongly scatter light. The lattice constant has been specifically chosen to produce photonic bandgaps in the visible spectrum, and the dried crystals are highly opalescent due to diffracted visible light. At normal incidence, the films have a beautiful green-blue sheen to them, which, as will be explained further on, is due to a second order photonic stop-band at normal incidence.

Given the optical nature of the photonic crystals, optical measurements are possibly the most obvious and informative method of characterising our structures. With this in mind, we therefore designed and built an experimental set-up which allows us to characterise the optical transmission properties of our structures.

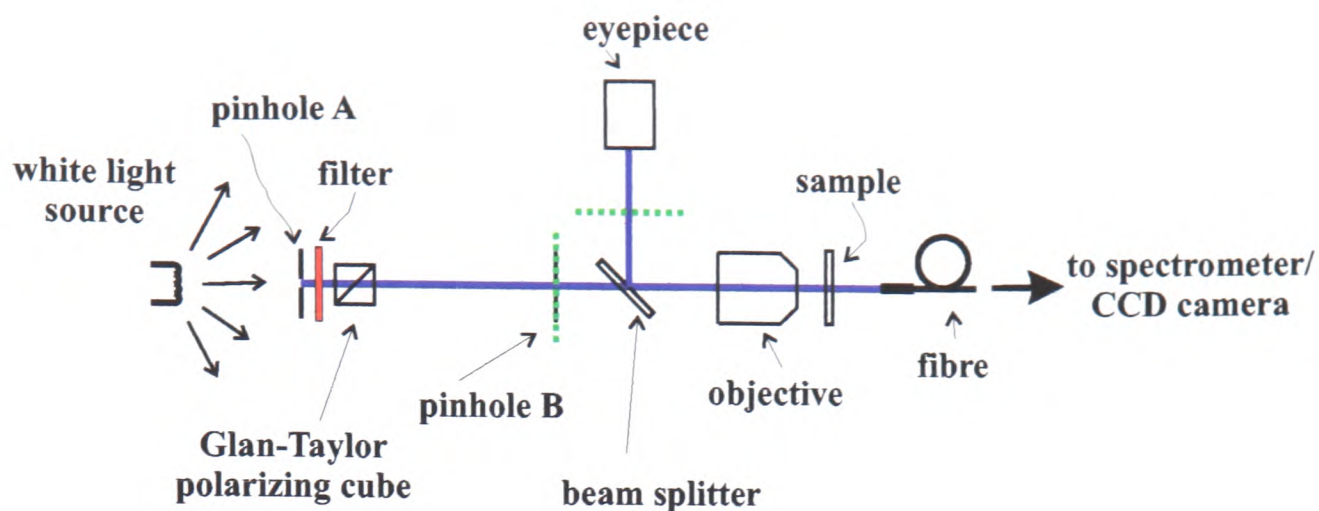


Figure 5.1: Schematic of the transmission microscope.

5.1 The Optical Characterisation Apparatus

Figure 5.1 shows a schematic of the microscope we designed to measure the optical transmission of our photonic crystals. The transmitted light is collected by an optical fibre, dispersed in a spectrometer and then captured on a Si CCD array. Figure 4.11 suggests that in the $[111]$ direction, the film normal, a first transmission gap occurs around $\sim 900\text{ nm}$. A Si CCD detector chip, with a cut-off wavelength at $1.12\text{ eV} = 1060\text{ nm}$, the silicon direct bandgap, is therefore ideally suited to our application. Since our photonic crystal structures have been specifically designed for the visible spectrum, the short wavelength cut-off of the transmission spectra is set at 400 nm . This wavelength range is free from atmospheric absorption features, which only start to become significant around 1400 nm [96]. The choice of wavelength range simplifies the experimental set-up as we do not need to purge the microscope with an inert gas.

An extended white light source produces an intense continuous spectrum from 400 nm to well into the infrared. Two variable-diameter irises, separated by 225 mm , ensure that the incident light is effectively ‘collimated’. A long-working distance objective focuses the light onto the sample; an eyepiece with a graticule images the sample so that we

can visually align the focussed spot onto an area of the sample. Aperture A controls the angular spread of the cone of light at the objective's back-focal plane, and hence at the sample. Aperture B, in the graticule plane, is imaged onto the sample and hence controls the diameter of the incident beam on the sample. A neutral density filter, positioned at an angle of 45° with respect to the incident beam, acts as a beam splitter so that the sample can be imaged at the graticule plane. Sufficient light is reflected from the sample to the eyepiece that we can visually align the sample.

The objective is a long working distance achromat (working distance 15 mm ; focal length 17 mm) with a magnification of 10. The quoted numerical aperture of the lens is 0.18, leading to a half angle of 10° for the incident cone of light. The spread of incident wavevectors in such a cone of light is too high, and we need to reduce the numerical aperture of the experiment. The incident beam does not fill the backfocal plane of the objective and can be stepped down by reducing the size of aperture B, which in turn will reduce the numerical aperture of the experiment. The lens diameter is 4 mm , the beam diameter at the back focal plane only 1 mm . As a result, the numerical aperture at the sample is equal to $\sin(\arctan(0.25 \tan 10^\circ)) = 0.05$, which corresponds to an acceptable half angle of 2.5° . The depth-of-focus is

$$D_f = \frac{\lambda}{\text{NA}^2} \quad (5.1)$$

where λ is the wavelength and NA the numerical aperture. Nominally, the objective has a numerical aperture of 0.18, which leads to a depth-of-focus of $12\text{ }\mu\text{m}$ at $\lambda = 400\text{ nm}$ and a depth-of-focus of $33\text{ }\mu\text{m}$ at 1060 nm . This is perfectly adequate for this experiment since these values are comparable to our sample thicknesses.

In a single transmission measurement, the film is probed at a single incident angle over the entire wavelength range. The importance of flat, wrinkle-free samples on the scale of

the incident beam, already discussed in section 3.6, must therefore be emphasised. If the sample is not uniform over the area being probed, then effectively we probe the film over a range of incident angles in a single measurement. This can lead to broadening of the transmission dips to the extent that features can no longer be identified. The samples mounted on microscope coverslips appear to be flat on the scale of the illuminated spot on the sample (diameter $27\ \mu\text{m}$) when viewed in the eyepiece. A better measure of the uniformity of the sample over the area being probed is to compare transmission spectra of an ordinary air-dried film and a flat film. We found that transmission minima corresponding to photonic bandgaps could not be distinguished in a normal air-dried film.

The design of the sample stage is critical to the success of the transmission experiments. We wish to rotate the sample about a vertical axis lying in the (111) plane, which corresponds to the film surface, to scan the incident wavevector across the Brillouin Zone boundary. We must also ensure that the incident wavevector does not physically wander across the sample while it is being scanned across the Brillouin Zone boundary. A sample mount obeying these requirements is shown in figure 5.2; it has eight adjustments in total. The optic axis and the focal plane of the objective are fixed in space. The translation adjustment labelled 1 in figure 5.2 enables us to adjust the position of the mount so that the rotation axis of the mount, which runs parallel to arrow 4, intersects with the optic axis of the experiment. The translation adjustment labelled 2 enables us to position the rotation axis of the mount so that it intersects with the focal spot along the optic axis. This prevents the focal spot from travelling across the sample as the sample is rotated and hence ensures that we are always probing the same sample area. The rotation stage, labelled 3, allows us to rotate the sample and probe the same area

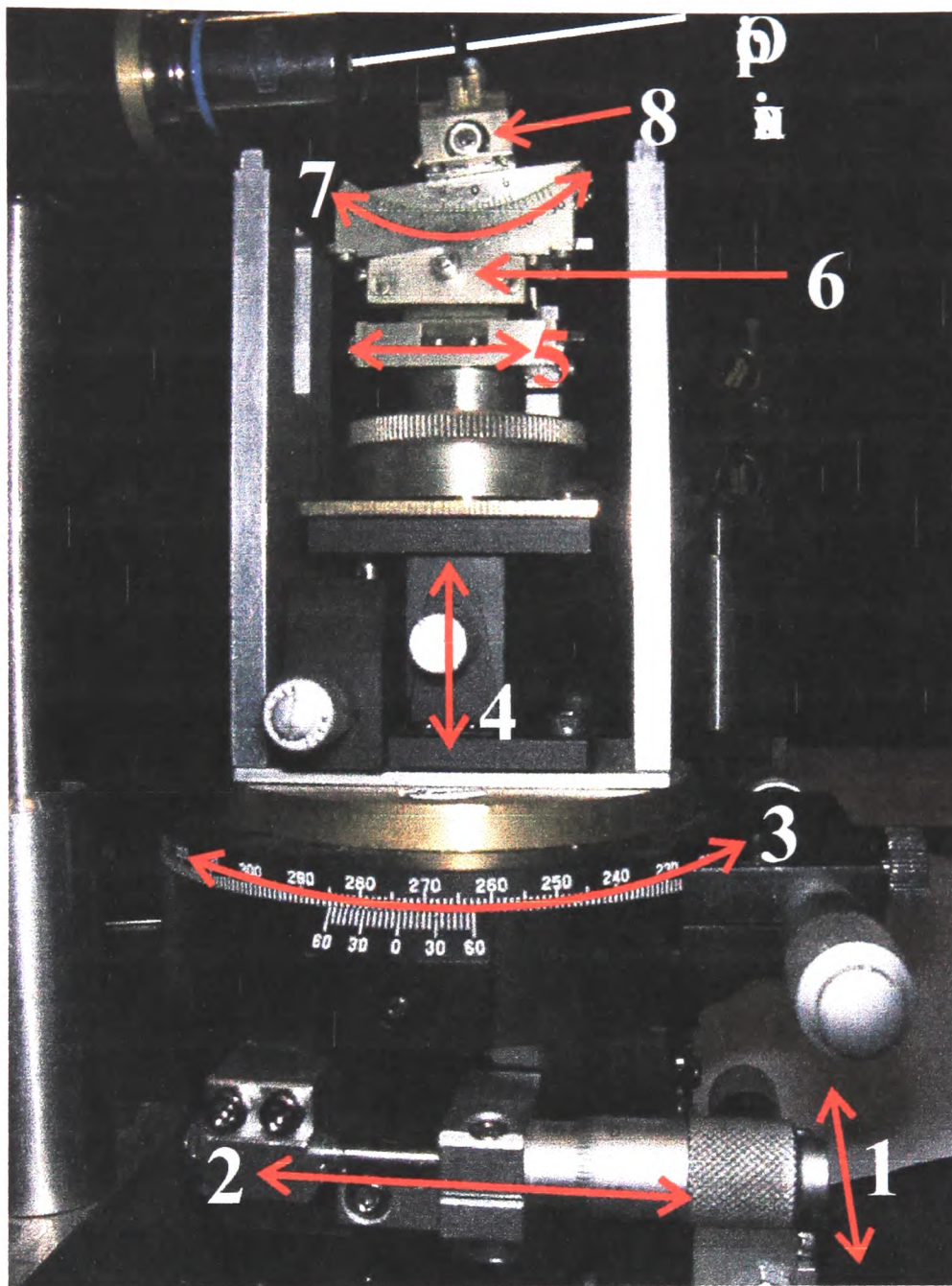


Figure 5.2: The sample mount in the transmission experiment has eight adjustments, which are numbered.

of the sample at different incident angles. The translation stage, labelled 4, allows us to scan the focal spot across the sample in the z-direction. Adjustment 5 allows us to translate the sample into the focal spot. Adjustment 6 allows us to scan the focal spot across the sample. The lower tilt adjustment (7) allows us to tilt the sample so that the area illuminated by the focal spot is normal to the optic axis. Finally, the upper tilt adjustment (8) enables us to rotate the sample around the optic axis so that when we scan across the sample, we are scanning along known symmetry directions. It is very important to emphasise that this sample mount has been designed to ensure that when probing the sample at different angles or along different symmetry directions, the axis of rotation are centred on the focal spot, and it is always the same area of sample that is probed.

How do we tell if the sample is at the focal spot, the tilt adjustment for adjusting the probe area normally to the optic axis and if the area we are probing has no visible defects? The neutral density filter inside the objective housing acts as a beam splitter/reflector. The reflection from the sample surface can therefore be observed with an eyepiece, positioned normally to the optic axis, which images the real plane rather than the Fourier plane. A graticule in the eyepiece with a series of centred, concentric circles allows us to measure diameters and radii. It was calibrated by printing a series of parallel lines on a piece of paper, each separated by a known, equal distance. In other words, we are relying on the calibration of the ink jet printer to calibrate the graticule. Based on these measurements, the inner circle has a radius of $27\text{ }\mu\text{m}$. We can focus on both the film surface and the cover slip surface. The sample tilt is adjusted by ensuring that the entire illuminated area is in focus at the same time. When the sample tilt is incorrectly adjusted, the illuminated area is not all in focus at the same time, so the edges on one

half of the area are blurred whilst the other edges are sharp.

We use a Princeton Instruments Spec-10:256E CCD camera to capture the spectra. The CCD chip consists of a spectroscopic-standard 1024x256 imaging array. The CCD is a front-illuminated detector with good quantum efficiency in the UV. This avoids all the associated problems with back-illuminated devices such as etaloning. The silicon CCD chip has a cut-off wavelength of $1.12\text{ eV} = 1060\text{ nm}$. The detector is Peltier-cooled down to -50°C , which effectively minimises any dark current in the system.

After passing through the sample, the light is captured in a multimode, wide-core single fiber, which is coupled into an Acton Research Corporation 308-i Spectrograph. We use two gratings, a 1200 lines/mm ruled grating blazed at 300 nm with a spectral range of 200 to 700 nm and a 600 lines/mm ruled grating, blazed at 1000 nm , with a spectral range of 660 to 2000 nm . We scan from 400 to 700 nm , using the 1200 lines/mm grating, and from 660 to 1060 nm with the 600 lines/mm grating. Below 400 nm , there is no discernible light above the background noise level. We therefore do not need to worry about second order effects until we reach 800 nm . In the 660 to 1060 nm scan, we filter out all second order effects with a red filter, which cuts out all wavelengths below 645 nm .

A software controlled shutter on the entrance slit allows us to control the exposure time. We use WinSpec, a proprietary, Microsoft Windows based real-time data acquisition and manipulation software for spectroscopic applications with full control of the camera, the shutter and the spectrometer.

5.2 Sample Orientation

The sample orientation is critical to understanding the transmission measurements. We would like to ensure that when the sample is rotated, the wavevector of the incident beam is scanned along a known direction in reciprocal space. The (111) plane, which corresponds to the film surface, has a hexagonal structure. There are two high-symmetry directions along which we would like to scan, along a line connecting two neighbouring basis and along the bisector of two such lines.

When the photonic crystal is probed by white light, six green-blue spots can be seen on the edge of the coverslip the photonic crystal is mounted on. These spots are separated by $\sim 60^\circ$, i.e. they have six-fold rotational symmetry about the [111] axis. They can be explained in a simple Bragg scattering model. The (111) plane spacing leads to a fundamental gap in the transmission spectrum at $\sim 1000\text{ nm}$ (the exact spacing is sample dependent), and a second order gap at $\sim 500\text{ nm}$, which appears green-blue to the naked eye. At the Brillouin zone boundary in the [111] direction, two further sets of planes are degenerate at the $2L_3$ point apart from the (222) plane: {200} and {220} type planes. The diffraction spots observed in the coverslip plane arise when the incident white light is Bragg scattered from the (200), (020), (002), (220), (202) and (022) planes.

Figure 5.3 shows a diagram of the Bragg scattering from the (200) and (220) planes. Let θ be the Bragg scattering angle: $\theta_{(200)} = 54.7^\circ$ and $\theta_{(220)} = 35.3^\circ$. The (200) plane scatters the light back towards the film surface, whereas the (220) plane scatters the light forward. The critical angle at the coverslip-air interface is $\theta_c = \arcsin(1/1.50) = 42^\circ$ (the coverslip is borosilicate glass); the angle of incidence of the scattered light at the coverslip-air interface is $70.6^\circ > \theta_c$. The light diffracted by the (220) plane therefore undergoes total internal reflection at the coverslip-air interface and eventually emerges

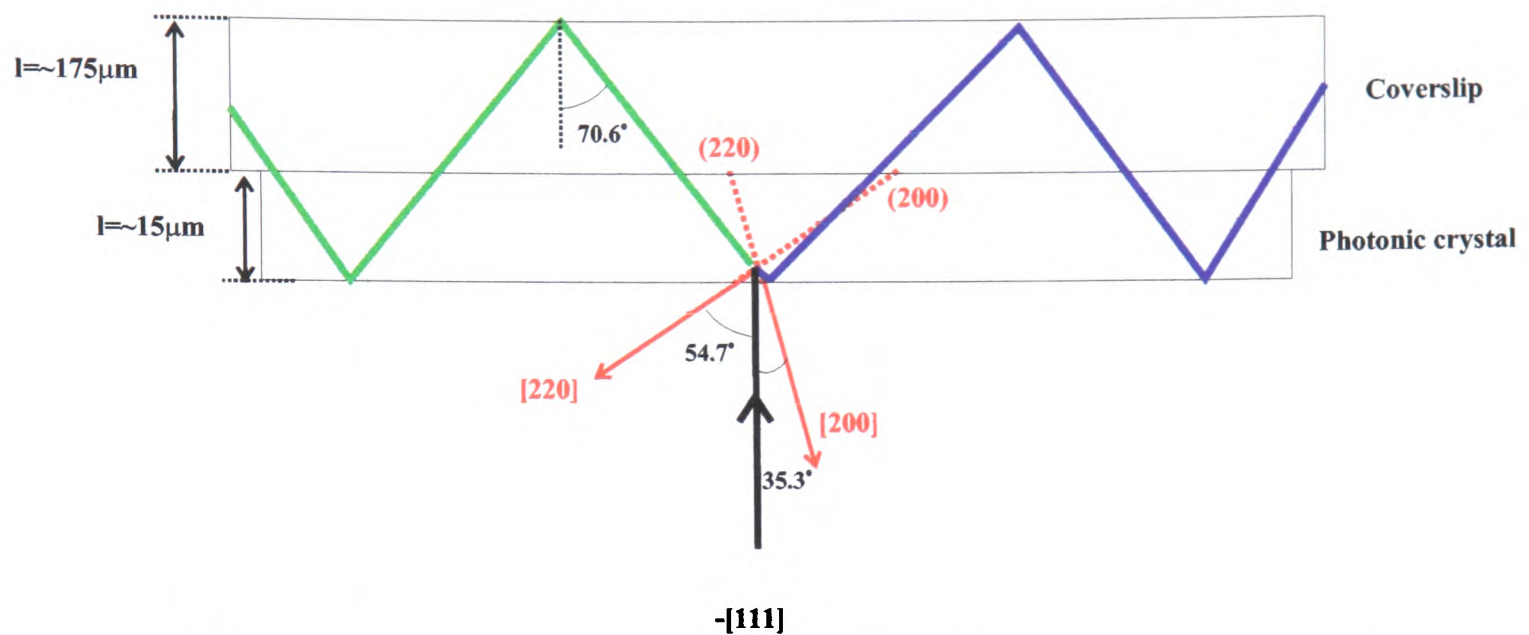


Figure 5.3: The schematic shows the origin of the diffraction spots used to align the photonic crystal for transmission measurements. Six green-blue diffraction spots are observed along the edge of the coverslip the photonic crystal is mounted on. These diffraction spots arise when the incident white light (black arrow labelled $-[111]$) is Bragg scattered off the $\{200\}$ and $\{220\}$ planes. The (220) plane scatters the light forward; it is reflected off the back surface of the coverslip and undergoes total internal reflection, eventually emerging along the coverslip edge. The (200) plane scatters the light backwards onto the front surface of the sample. Some of the light is scattered back, reflected off the back surface of the photonic crystal, again undergoes total internal reflection and eventually emerges through the coverslip edge.

through the coverslip edge, as shown by the green line in figure 5.3. Some light scattered by the (200) plane is reflected at the photonic crystal-air interface. The reflected light then undergoes total internal reflection at the coverslip-air interface and again eventually emerges through the coverslip edge, as shown by the blue line in figure 5.3. Although the two beam paths have been marked in different colours, the scattered wavelength is the same for both planes. I have also ignored any refraction of the light at the photonic crystal-coverslip interface. As I will show in section 5.3, the average refractive index of the sample in the Bragg model is 1.48. The refractive index of the borosilicate glass coverslip is 1.50, which is close enough to that of the sample in this instance to ignore.

Let us now consider how to determine the relationship between the symmetry direction along which we scan and the pattern of diffraction spots. The blue arrows in figure 5.4 mark the projections of [200], [020] and [002] onto the (111) plane, which is parallel to the plane of the coverslip. The green arrows mark the projection of the [220], [202] and [022] reciprocal lattice vectors onto the (111) plane. The six-fold rotational symmetry of the diffracted spots arises naturally from this geometry. The (111) face of the first Brillouin Zone boundary is marked in a dotted line, and the symmetry points L_3 , U_3 , K_3 and W are marked. The subscript denotes that the axis normal to the plane, passing through L_3 is a threefold rotation axis; the notation convention follows that laid out by Yablonovitch in [21]. From this simple diagram, we deduce that if the sample is orientated such that the incident wavevector is scanned along the line bisecting the angle between two diffraction spots, then we are essentially scanning from L_3 (normal incidence) out to U_3 or K_3 . When the scan line passes through a diffraction spot, we are scanning from L_3 out to W and beyond.

I will refer to the two different orientations as the α orientation ($U_3 \leftrightarrow L_3 \leftrightarrow K_3$) and

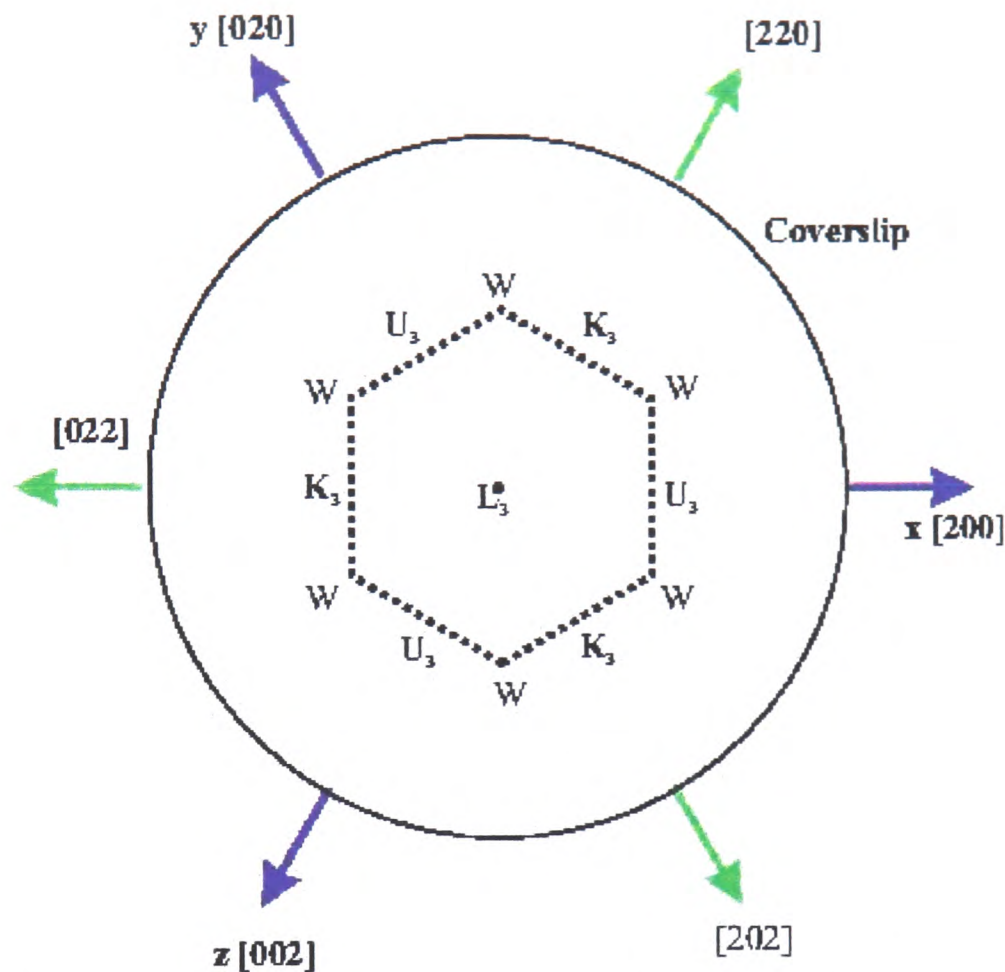


Figure 5.4: The light diffracted out of the edge of the coverslip on which the photonic crystal is mounted is shown schematically in the (111) plane, which corresponds to the sample surface. The spots correspond to Bragg scattered light off the 200 and 220 type planes and can be used for sample alignment. The blue arrows mark the projection of the reciprocal lattice vectors of the (200) type planes onto the (111) plane; the green arrows the projection of the reciprocal lattice vectors of the (220) type planes onto (111). When wavevectors of the incident white light beam are scanned along a line connecting two diffraction spots, they are scanning along a line connecting L_3 to W . When the incident wavevectors are scanned along a line bisecting the angle subtended by two diffraction spots, they are scanning along a line connecting L_3 , U_3 and K_3 .

the β orientation ($W \leftrightarrow L_3 \leftrightarrow W$). We would expect the transmission data obtained by scanning a set of incident wavevectors in the α orientation to be asymmetric about normal incidence whereas the transmission data obtained when the sample is scanned in the β orientation is expected to be symmetric about normal incidence.

5.3 Optical Transmission Spectra and the Bragg Model

Experience has shown that it is possible to tell a good film visually by its milky-white appearance and uniform green-blue colour in transmission.

Transmission spectra of a photonic crystal exposed to the non-chiral face-centred cubic pattern with a lattice constant of 922 nm in air, mounted on a microscope coverslip, were recorded over an external incident angle range of -80° to $+80^\circ$ for both s and p incident polarisations in both the α and β scan orientations. The spectra were normalised by dividing through by the corresponding spectrum taken through air. I found that the coverslip itself had no appreciable effect on the spectra.

Figure 5.5 shows three normalised spectra for s incident polarisation, taken at normal incidence, and with an angle of incidence 35° and 50° out towards the K_3 direction. Distinct minima in transmission are visible; the wavelength of these features moves as the external angle of incidence is increased. These features represent stop bands. The Bragg scattering planes responsible for the features are indicated in the figure; I will describe in the following paragraphs how to assign plane indices to the features. The fundamental gap in the (111) direction is centred at 963 nm and shows a dip in transmission from 50% to 10%. The full-width at half maximum is 35 nm , which corresponds well with the gap between band edges deduced from bandstructure calculations as shown in figure 5.5.

The normalised data were differentiated over a moving window of 10 data points, and

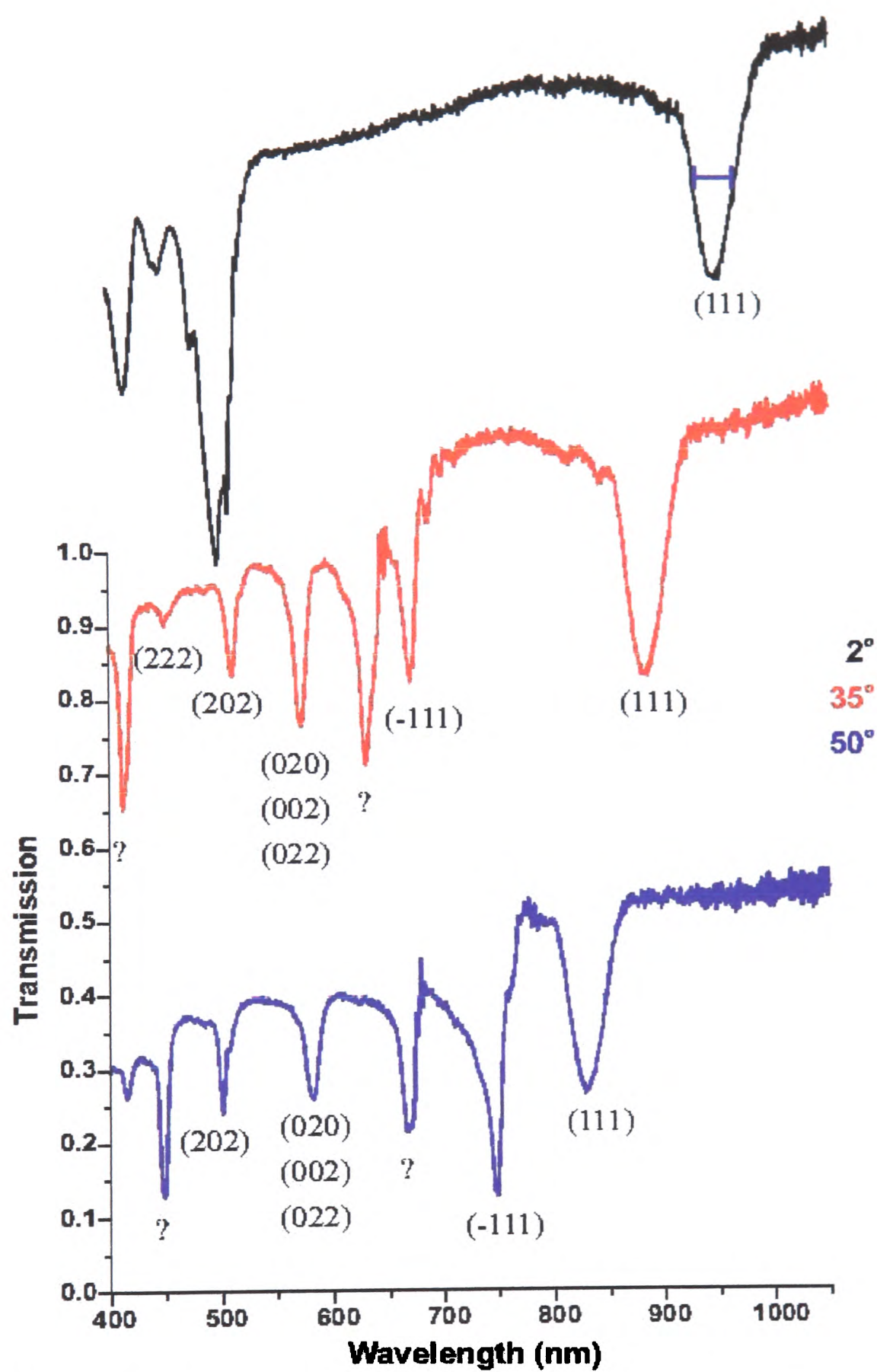


Figure 5.5: Normalised transmission spectra at three external incident angles show sharp dips in the optical transmission through a face-centred cubic sample. The scattering planes responsible for the features have been marked; several features cannot be identified.

the gap centres were taken to be the wavelengths where the slope changed from negative to positive values. The data resolution is 0.5 nm , so any features narrower than 5 nm will not be picked up with this method. The smoothing was necessary to reduce jitter on the data and minimise artefacts, but a visual check showed that no obvious features were excluded.

Figures 5.6 and 5.7 show the gap centres as a function of external angle for s polarised incident light in both sample orientations. To understand the movement of these gaps and identify the features, I assume in the first instance that the incident light undergoes simple Bragg scattering inside the crystal and use an average refractive index to calculate the Bragg scattering angles. This model assumes weak scattering and would be most appropriate for a photonic crystal with a vanishingly small refractive index contrast. Nevertheless, the Bragg scattering model gives us a useful handle to interpret the features observed in the transmission spectra. In section 5.5, I reinterpret the data using photonic bandstructure calculations and compare the two models.

We use the von Laue formulation for scattering by a crystal to identify the scattering planes [10]:

$$\mathbf{k} \cdot \mathbf{G} = \frac{1}{2}|\mathbf{G}|^2 \quad (5.2)$$

where $\mathbf{k}$ is the incident wavevector and $\mathbf{G}$ is a reciprocal lattice vector. A wavevector which satisfies the von Laue condition can be regarded as Bragg reflected from the family of direct lattice planes perpendicular to the reciprocal lattice vector $\mathbf{G}$. The family of Bragg planes is labelled with $\mathbf{G}$.

Furthermore, we know that, in the case of weak scattering, the amplitude of the scattered light will be proportional to the structure factor [10]. In the case of a face-centred cubic structure, the structure factor is non-zero only if the reciprocal lattice

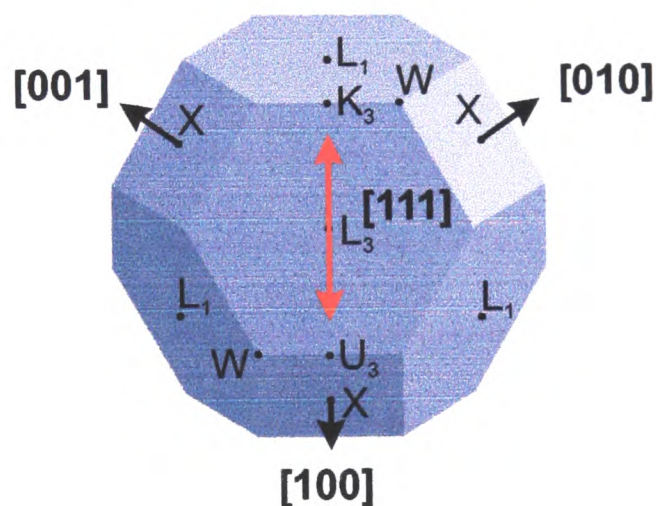
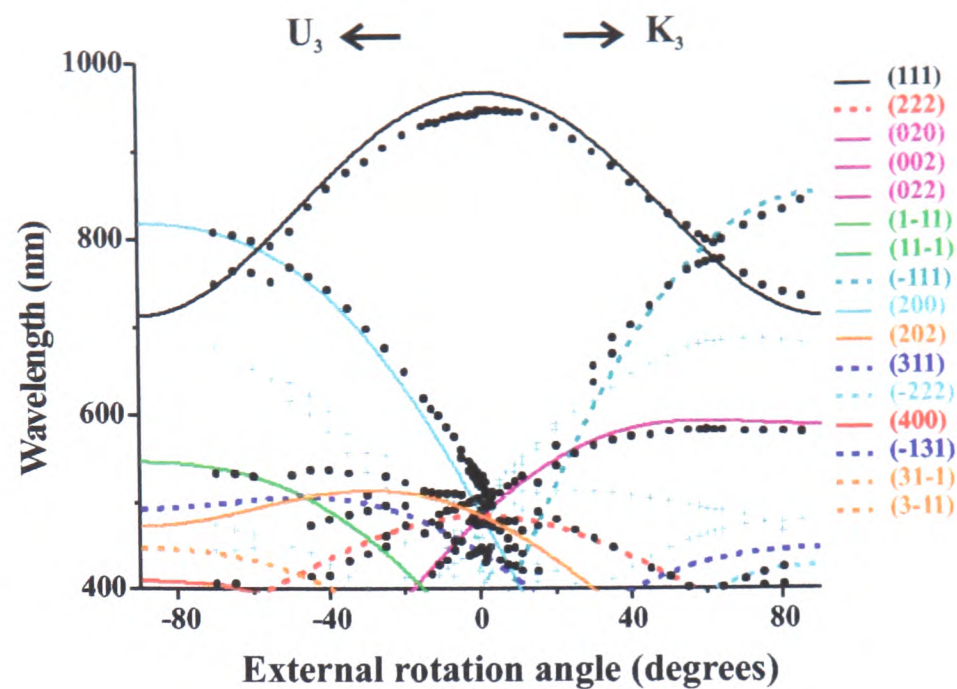


Figure 5.6: Transmission gaps are plotted as a function of external incident angle. The sample is orientated so that the scan plane passes through the U_3 , L_3 and K_3 high symmetry points. The scan direction is indicated with an arrow on the first Brillouin zone boundary at the bottom of the figure. The data has been fitted with simple Bragg scattering planes. There are some features which we have not been able to identify.

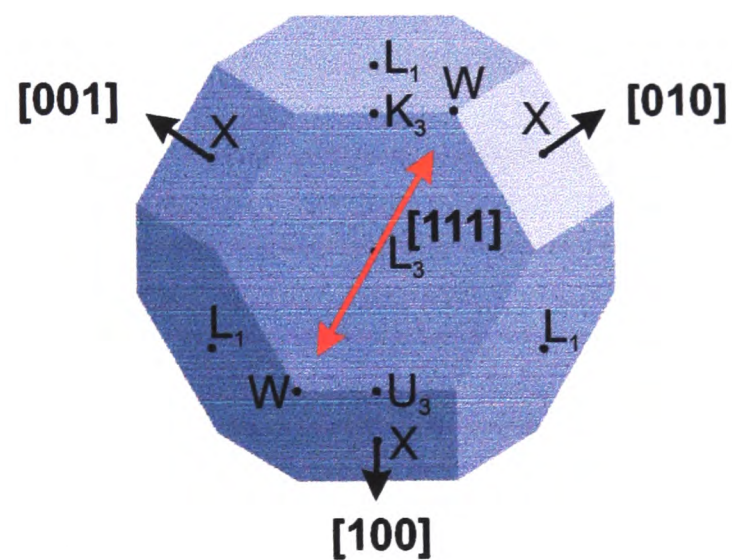
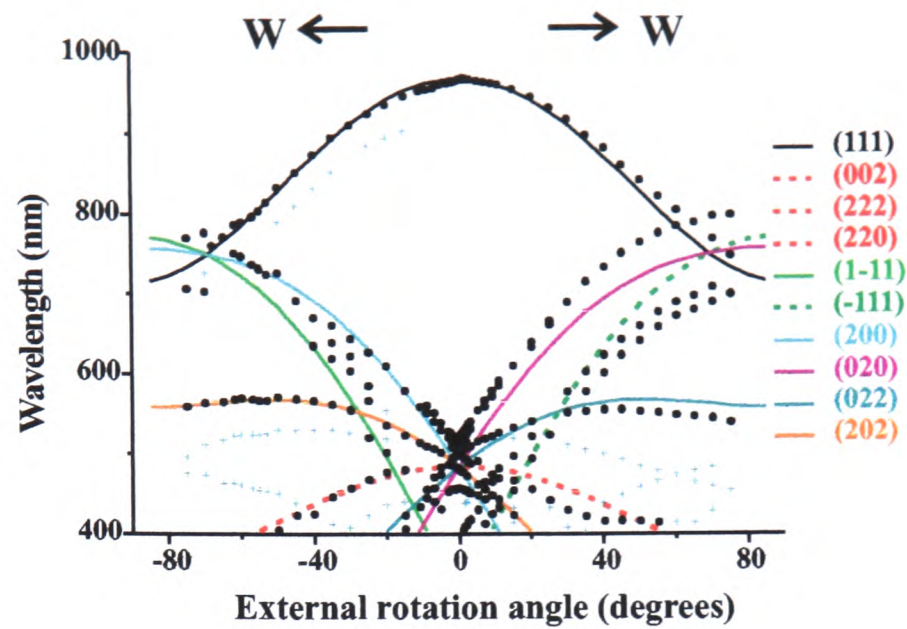


Figure 5.7: Transmission gaps are plotted as a function of external incident angle. The sample is orientated so that the scan plane passes through the W , L_3 and W high symmetry points. The scan direction is indicated with an arrow on the first Brillouin zone boundary at the bottom of the figure. The data has been fitted with simple Bragg scattering planes. Again there are some features which we have not been able to identify.

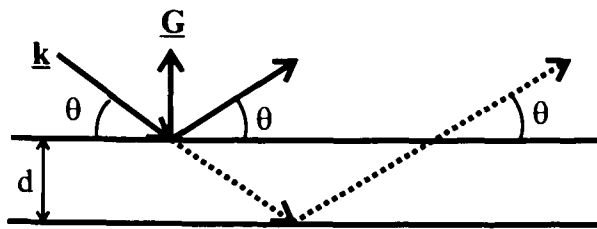


Figure 5.8: The schematic shows Bragg scattering from a set of parallel crystal planes with reciprocal lattice vector $\mathbf{G}$.

vector has either all even or all odd Miller indices. So only a $\mathbf{G}$ with either all even or all odd Miller indices has an associated Bragg reflection.

To fit the data, I use the conventional three-dimensional Bragg formula for scattering [10]:

$$\lambda = 2n_{av}d \sin\theta = 2n_{av} \frac{a}{\sqrt{h^2 + k^2 + l^2}} \sin\theta = 2n_{av} \frac{a}{\sqrt{h^2 + k^2 + l^2}} \hat{\mathbf{k}} \cdot \hat{\mathbf{G}} \quad (5.3)$$

where n_{av} is the average refractive index, a the conventional cube side, (h, k, l) the Miller indices of the plane, θ the conventional Bragg angle, $\hat{\mathbf{G}}$ the normalised reciprocal lattice vector and $\hat{\mathbf{k}}$ the normalised incident wavevector within the photonic crystal, as illustrated in figure 5.8.

In the above equation, I need to reformulate $\hat{\mathbf{k}}$ in terms of an experimentally measured parameter, which is the angle by which the photonic crystal has been rotated from normal incidence, measured in the scan plane. The scan plane is defined by $[111]$, the sample normal, and by the incident wavevector $\hat{\mathbf{k}}$, which fulfills the Bragg scattering condition. I will label the scan plane with the vector normal $\mathbf{p} \in (111)$. Let us consider the intersection of the Brillouin zone boundary with the scan plane, as shown in figure 5.9. ϕ is the angle between $\mathbf{k}$ and the vector $[111]$ normal to the sample, after refraction at the air-sample interface; $\mathbf{k}_0$ is the wavevector which fulfills the Bragg condition for this particular Brillouin zone boundary at normal incidence ($\phi = 0^\circ$, so $\mathbf{k}_0$ is parallel to $[111]$).

Figure 5.9 shows that, when the Bragg condition is met, the incident wavevector can

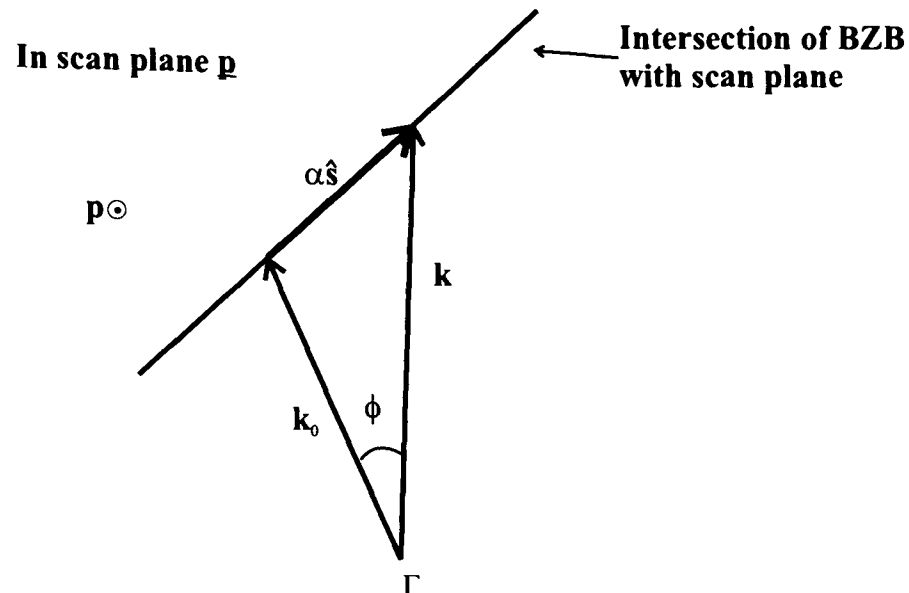


Figure 5.9: The schematic shows the intersection of a Brillouin zone boundary with the scan plane. The vectors required in the Bragg formulation are marked on the schematic. ϕ is the refracted measured incident angle.

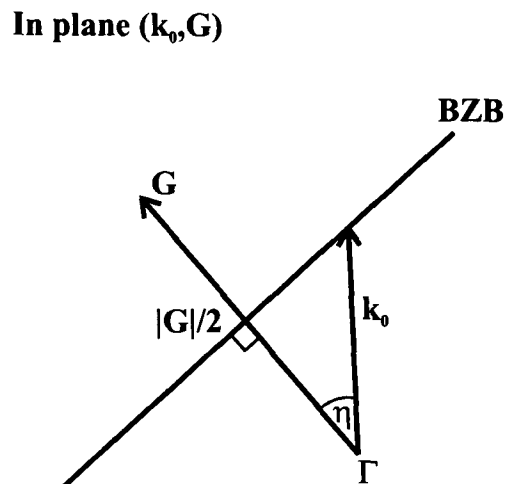


Figure 5.10: The schematic shows the Brillouin zone boundary in the plane defined by the wavevector which fulfills the Bragg condition for this Brillouin zone boundary at normal incidence and the reciprocal lattice vector. The vectors required in the Bragg formulation are marked on the schematic.

be rewritten as:

$$\mathbf{k} = \mathbf{k}_0 + \alpha \hat{\mathbf{s}} \quad (5.4)$$

where $\mathbf{k}_0$ is the wavevector which meets the Bragg condition at normal incidence and is hence parallel to $[111]$. $\hat{\mathbf{s}} = \frac{\mathbf{p} \wedge \mathbf{G}}{|\mathbf{p} \wedge \mathbf{G}|}$, and $\alpha = f(\phi)$ is a function of the refracted measured incident angle ϕ . Since ϕ is the angle between $\mathbf{k}_0$ and $\mathbf{k}$, α can be determined by using the relationship:

$$\cos\phi = \frac{\mathbf{k}_0 \cdot (\mathbf{k}_0 + \alpha \hat{\mathbf{s}})}{|\mathbf{k}_0| |\mathbf{k}_0 + \alpha \hat{\mathbf{s}}|} \quad (5.5)$$

Finally, we need an expression for $\mathbf{k}_0$. Figure 5.10 shows that:

$$\begin{aligned} \mathbf{k}_0 &= |\mathbf{k}_0| \hat{\mathbf{k}}_0 \\ &= \frac{|\mathbf{G}|}{2} \frac{1}{\cos\eta} \hat{\mathbf{k}}_0 \end{aligned} \quad (5.6)$$

where

$$\cos\eta = \frac{\mathbf{G} \cdot \hat{\mathbf{k}}_0}{|\mathbf{G}|} \quad (5.7)$$

Hence:

$$\mathbf{k}_0 = \frac{|\mathbf{G}|^2}{2} \frac{\hat{\mathbf{k}}_0}{\mathbf{G} \cdot \hat{\mathbf{k}}_0} \quad (5.8)$$

$\hat{\mathbf{k}}_0$ is a unit vector in the direction of $[111]$. Using this formulation, we fitted the data in figures 5.6 and 5.7.

When fitting the data in the Bragg model, there are two parameters at our disposal: the fill fraction or ratio of material to void in the structure, from which we calculate the average refractive index, and the cube side a . The best fit is achieved when the cube side is set to the ideal lattice constant of the original interference pattern in SU-8, 566 nm , which then leads to a fitted average refractive index of $n_{av} = 1.48$. From this fitted volume-averaged dielectric constant, we can deduce the fill fraction of the structure from

$$n_{av} = 1.48 = \sqrt{(1 - \alpha) \epsilon_{air} + \alpha \epsilon_{SU-8}} \quad (5.9)$$

where $\epsilon_{SU-8} = 1.63^2$ is the dielectric constant of SU-8, and $\epsilon_{air} = 1$ is the dielectric constant of air. From this we infer that $\alpha = 72\%$ is the fill fraction. IDL calculations of isosurfaces, discussed in section 4.1.2, show that the non-chiral interference patterns have a network of interconnected voids and interconnected material for fill fractions in the range 22% to 79%. An inferred fill fraction of 72% is therefore entirely reasonable. A fill fraction at the high end of the allowed range is in fact advantageous as the photonic crystal is more robust and better able to withstand any handling it undergoes during adhesion to a coverslip.

During polymerisation, the photonic crystal tends to shrink, and the plane spacing in the crystal is typically 90% of that in the interference pattern. This contradicts the optical transmission data to some extent. A 10% shrinkage in the lattice constant leads to a fitted average refractive index of $n_{av} = 1.64$, which is greater than that of SU-8. This implies that the sample does not shrink as much as the samples, which were imaged in the scanning electron microscope, or that the calibration in the electron microscope is out.

Refraction at the air-sample interface limits the range of internal angles we can probe. The critical angle at the air-sample interface is $\arcsin(1/1.48) = 42^\circ$ if the effective refractive index is 1.48, which represents the largest internal angle we can probe. The data show that we just cross from the (111) plane to the (200) and ($\bar{1}11$) planes on the first Brillouin zone boundary in the α orientation and through the W points to the ($\bar{1}11$) and ($1\bar{1}1$) planes in the case of the β orientation (c.f. figures 5.6 and 5.7).

5.4 Unassigned Features in the Transmission Spectra

In figures 5.6 and 5.7, some of the data has been represented by crosses. These features remain unidentified in the Bragg picture. We have investigated several explanations for these features, but have not succeeded in explaining them to our satisfaction.

The most immediate explanation is that some Bragg planes, disallowed in the face-centred cubic rules, are scattering light; in other words, the structure is not truly face-centred cubic. Having rerun the algorithm without the restriction that the Miller indices of the Bragg planes must be either all odd or all even (the face-centred cubic scattering rule), the features can still not be assigned to scattering from disallowed planes.

A second explanation is that the sample in the area probed was folded over or another piece of sample fell onto the area probed so that the incident wavevector was probing two samples simultaneously, one piece in the expected orientation, a second piece in an unknown orientation. If this is indeed the case, then the unassigned features in the transmission data can be understood if the Bragg planes obtained in the unknown sample orientation are superimposed onto the data already fitted.

We have examined one possible sample configuration in detail: two pieces of sample are simultaneously probed in the α - and β - orientations.

Figure 5.11 shows the U_3 - L_3 - K_3 scan superimposed on the W - L_3 - W scan. The dashed lines represent the Bragg fits from the U_3 - L_3 - K_3 scan and the solid lines the Bragg fits from the W - L_3 - W scan. In this instance, we expect to probe the sample along the Brillouin zone boundaries towards the W point. The unassigned features cannot be fitted by Bragg planes in the U_3 - L_3 - K_3 orientation, although qualitatively the trends of the

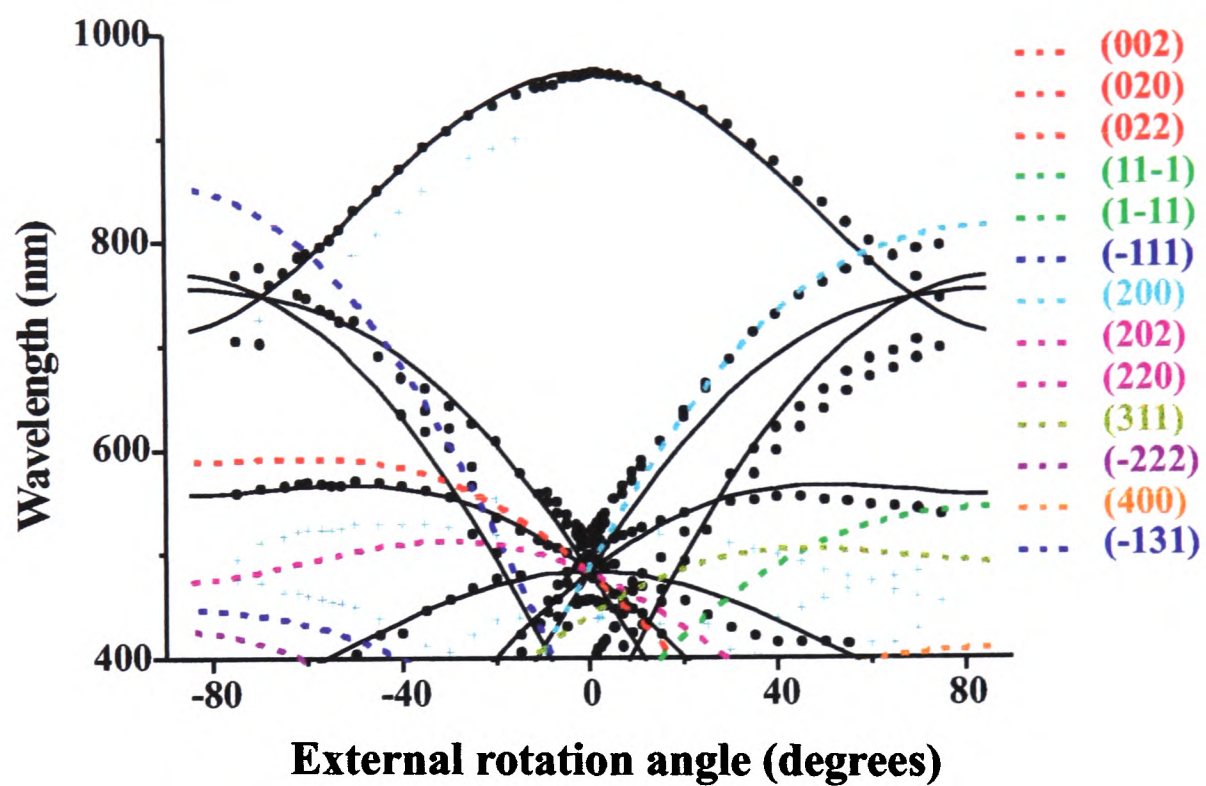


Figure 5.11: The Bragg planes from the U_3 - L_3 - K_3 scan orientation, marked by dashed lines, are superimposed on the data obtained in the W - L_3 - W scan orientation. The Bragg planes from the U_3 - L_3 - K_3 orientation do not fit the unassigned data, but they do match the trend of the unassigned data qualitatively.

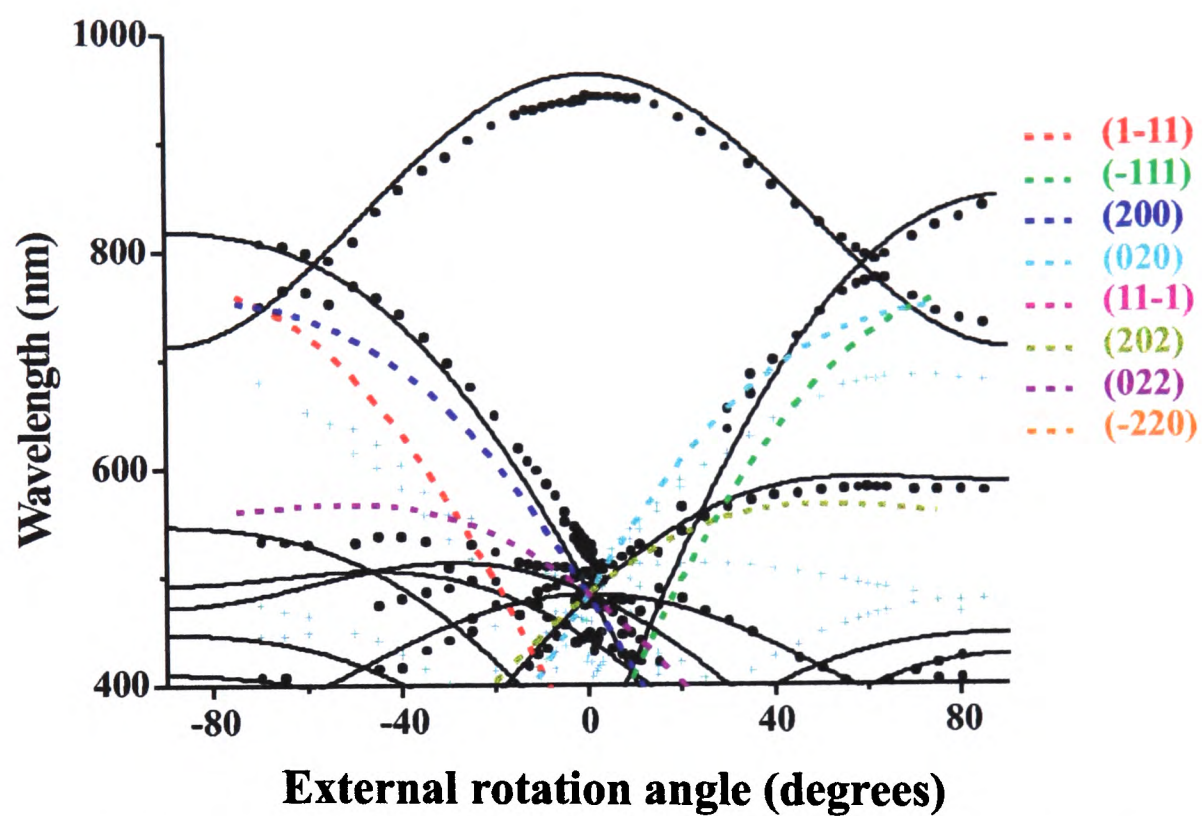


Figure 5.12: The Bragg planes from the W-L₃-W scan orientation, marked by dashed lines, are superimposed on the data obtained in the U₃-L₃-K₃ scan orientation. The Bragg planes from the W-L₃-W orientation do not fit the unassigned data.

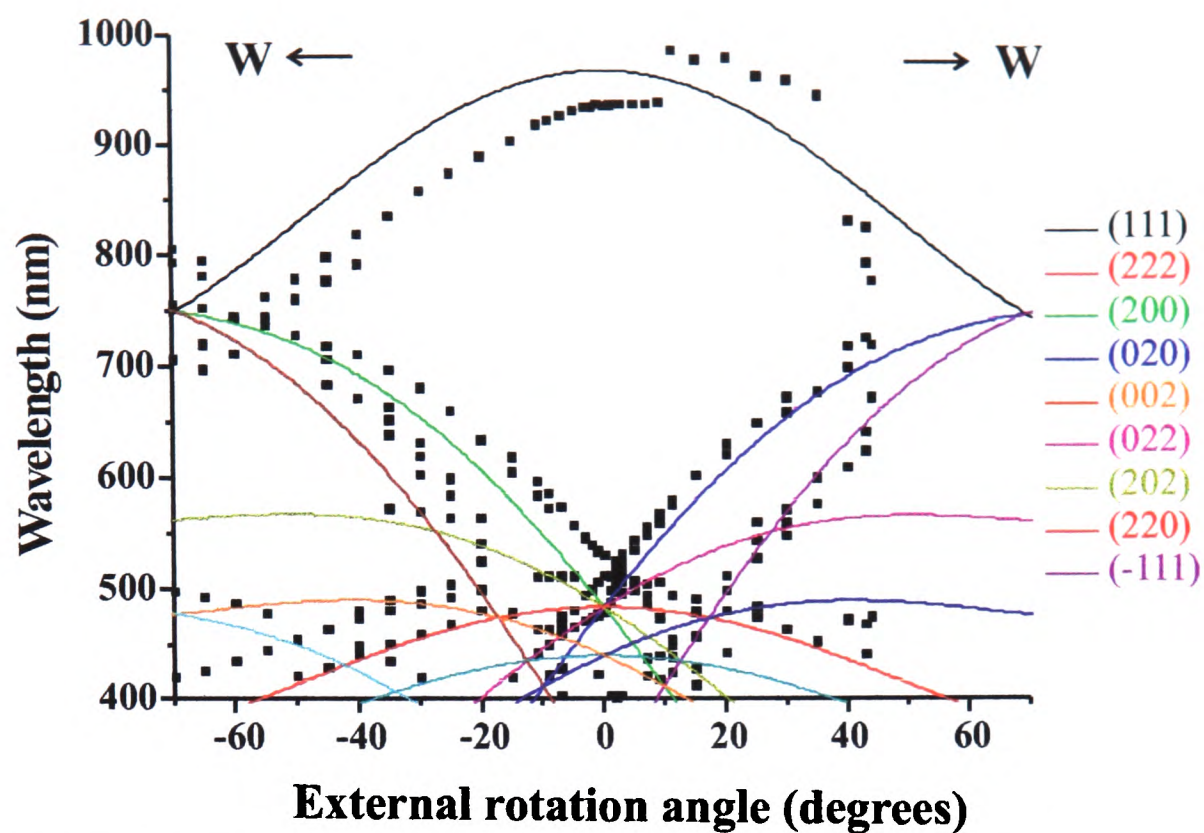


Figure 5.13: The transmission data from a second photonic crystal in the W-L₃-W orientation has no unassigned features.

unassigned features follow the Bragg planes from the alternative orientation reasonably well. Figure 5.12 shows the W-L₃-W scan superimposed on the U₃-L₃-K₃ scan. Again, the unassigned features are not fitted by the Bragg planes from the alternative orientation.

We can therefore rule out the possibility that two pieces of sample were being probed simultaneously in the α - and β - orientations. This does not however rule out the possibility that a second piece of sample was in some unknown orientation between the two high-symmetry orientations.

We do not, to date, have an alternative explanation for the occurrence of the unassigned features. They are unique to this sample; they are not present in two other photonic crystals generated with the same interference pattern. Figure 5.13 shows the transmission gaps plotted as a function of external incident angle for one of these samples in the W-L₃-W scan orientation and fitted with Bragg planes. The unassigned features

marked in crosses in figure 5.7 are no longer present in these transmission spectra. The additional photonic crystals were fabricated at a very late date, purely in order to check for unexplained features, so I have chosen not to analyse their transmission data in detail. Furthermore, the quality of these data is quite low, probably due to adhesion problems between the sample and the coverslip.

5.5 Interpreting the Transmission Spectra with Photonic Bandstructures

Although the Bragg model gives us a useful insight into the stopbands, it is an approximation as the Bragg picture is only valid for weak scattering whereas photonic crystals are inherently strong scatterers of light. A far better model for understanding the transmission through a photonic crystal, and one which reflects the physical situation, is to extract information on the stopbands from photonic bandstructure calculated for a periodic dielectric constant, as described in section 2.1.

The MIT MPB code was used to calculate the photonic bandstructure. The code requires as input the spatial distribution of the dielectric constant within the primitive cell of the structure. The IDL-generated isosurfaces are converted into a format suitable to be used as input for the MPB calculations, using a program created by Dr D. Sharp. Before starting these calculations, two pieces of information about the actual sample are required if the output of the calculations is to be compared with the transmission data: the fill fraction of the sample and its lattice constant. Both of these pieces of information can be extracted from the Bragg model; the data in figures 5.6 and 5.7 was fitted with a lattice constant of $a = 566 \text{ nm}$ and an average refractive index of $n_{av} = 1.48$,

which corresponds to a fill fraction of 72% as shown in equation 5.9. It is important to emphasise that both the fill fraction and the lattice constant used in the bandstructure calculations are chosen to have the same values as those used to fit the data in the Bragg model.

The output of the MPB code is the energy eigenvalues in units of hc/a , where $h = 6.626 \cdot 10^{-34} \text{ J s}$ is Planck's constant, $c = 2.998 \cdot 10^8 \text{ m s}^{-1}$ is the speed of light and a is the lattice constant, as a function of the refracted, i.e. internal, wavevector. The experimental data consists of transmission minima wavelengths as a function of incident, i.e. external, angle. In order to compare the photonic bandstructure calculations with the experimental data, we need to decide on sensible units in which to display both the data and the bandstructure calculations.

It follows from Snell's law that the component of the wavevector parallel to the interface is conserved when the wavevector is refracted into the sample (c.f. for example chapter 4.6.1 in [97]). In general, the incident wavevector can be decomposed into a linear combination of components parallel and perpendicular to the sample interface:

$$\begin{aligned} \mathbf{k}_i &= \mathbf{k}_{\parallel} + \mathbf{k}_{\perp} \\ &= |\mathbf{k}_i| \sin \theta_i + |\mathbf{k}_i| \cos \theta_i \end{aligned} \quad (5.10)$$

where θ_i is the measured, external angle of incidence. $\mathbf{k}_{\perp}$ cannot be deduced from experimentally measured parameters without prior knowledge of the bandstructure. Since $\mathbf{k}_{\parallel}$ is conserved across the interface, it can be deduced from measured parameters. I have therefore chosen to replot the transmission data in units of energy as a function of $\mathbf{k}_{\parallel}$ in

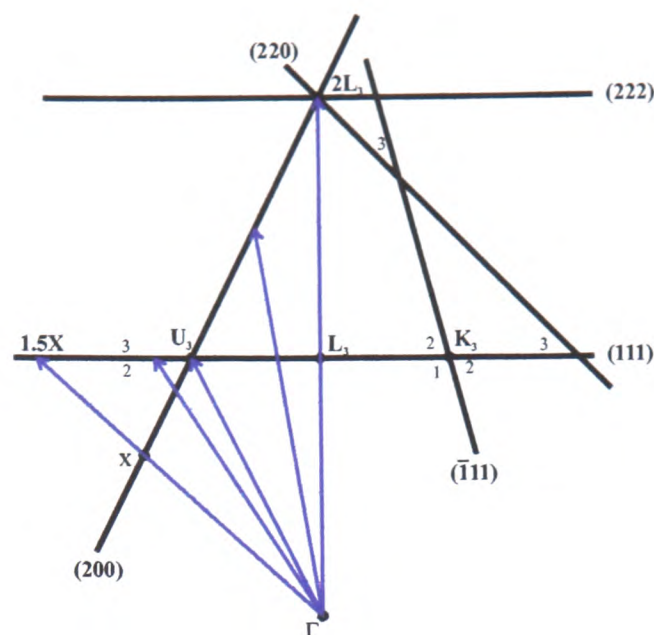


Figure 5.14: The intersection of the Brillouin zone boundaries, which correspond to Bragg planes, with the scan plane $(01\bar{1})$. The transmission gaps can be tracked as a function of incident wavevector angle by calculating bandstructures along specific trajectories (c.f. text for more detail).

figures 5.22 and 5.18. The energy eigenvalues can also be replotted in terms of $\mathbf{k}_{||}$, since

$$\begin{aligned} |\mathbf{k}_{||}| &= |\mathbf{k}_r| \sin \theta_r \\ &= |\mathbf{k}_r| \sqrt{1 - \cos^2 \theta_r} \end{aligned} \quad (5.11)$$

where

$$\cos \theta_r = \frac{\Gamma \mathbf{L}_3 \cdot \mathbf{k}_r}{|\Gamma \mathbf{L}_3| |\mathbf{k}_r|} = \frac{k_1 + k_2 + k_3}{\sqrt{3} |\mathbf{k}_r|} \quad (5.12)$$

k_1, k_2, k_3 are the coordinates of $\mathbf{k}_r$, the refracted wavevector. They are automatically calculated by the MPB code. θ_r is the refracted angle.

In order to track the movement of the transmission minima as a function of $\mathbf{k}_{||}$, the trajectories along which the photonic bandstructures are calculated need to be chosen carefully. As the von Laue condition shows, a gap in transmission is encountered when the incident wavevector encounters a Brillouin zone boundary. We can use our knowledge of

the Bragg planes associated with the stop bands to calculate the photonic bandstructure along a trajectory designed to follow the movement of one particular energy gap.

Figure 5.14 shows the intersection of Brillouin zone boundaries, which correspond to the Bragg planes, with the scan plane, when the sample is in the α orientation (so the scan plane is $(01\bar{1})$). The boundaries have been labelled with the corresponding reciprocal lattice vector; the zones have been numbered. I have only shown the first three boundaries and have chosen to display the zone boundaries only where required for the bandstructure calculations. The fundamental energy gap can be tracked as a function of angle if the photonic bandstructure is calculated along the trajectory $\Gamma-L_3-U_3-X$. An anti-crossing of gaps occurs at U_3 , where the Bragg plane responsible for the fundamental gap switches from the (111) plane to the (200) . To track the movement of the second energy gap in the same real-space direction, we need to calculate the photonic bandstructure along the trajectory $\Gamma-2L_3-U_3-1.5X$. The wavevectors shown in figure 5.14 lie on this trajectory.

The trajectory is chosen so that the movement of each bandgap is tracked continuously. In this trajectory, the second bandgap appears as a continuous energy gap between bands four and five. When tracking the movement of the third bandgap along a suitable trajectory, it will appear in the bandstructure calculations as a continuous energy gap between band six and seven and so on. A particular trajectory can hence be associated with each of the bandgaps. The photonic bandstructure needs to be recalculated for each of the trajectories.

The MPB code is ideally suited to calculating the bandstructure along such trajectories as we can directly input the Bloch wavevectors at which the bands need to be calculated. The code will automatically calculate the energy bands between two specified

Bloch wavevectors at a specified number of points (15 in this case).

This method of using the photonic bandstructure to track the movement of the transmission gaps relies heavily on the identification of the features in the Bragg model. If the features have been incorrectly assigned in the Bragg model, then the trajectory input into the photonic bandstructure will not follow exclusively the movement of one bandgap, and the method breaks down.

Figures 5.15 and 5.19 show a comparison between the data and the Bragg model for the two scan orientations; figures 5.16 and 5.20 display the data in the bandstructure picture for both scan orientations. Figures 5.17 and 5.21 compare the Bragg model and the bandstructure picture. The bars on the data show the full width at half minimum of the transmission features, where it was possible to extract this information. The bandstructure calculations have only been performed for the first four bandgap trajectories. At higher energy gaps, the trajectories become too complicated as too many zone boundaries intersect along these trajectories. These six figures are again shown in the composite figures 5.18 (the symmetric scan) and 5.22 (the asymmetric scan), which summarise the results of fitting the data with both the Bragg model and the bandstructure model.

Most interesting are the graphs comparing the Bragg fits and the bandstructure fits, shown in figures 5.21 and 5.17. The two models match up remarkably well for the first three bandgaps. For the fourth bandgap, the bandstructure fit is pushed to lower energies compared to the Bragg fit. I believe this is a result of the large number of Bragg planes intersecting at higher energies. Since the energy gaps do not cross, they are pushed apart in energy, which results in the fourth bandgap being pushed to lower energies than expected from the simple Bragg scattering model.

The bands in the calculated photonic bandstructure can be paired, each pair of bands

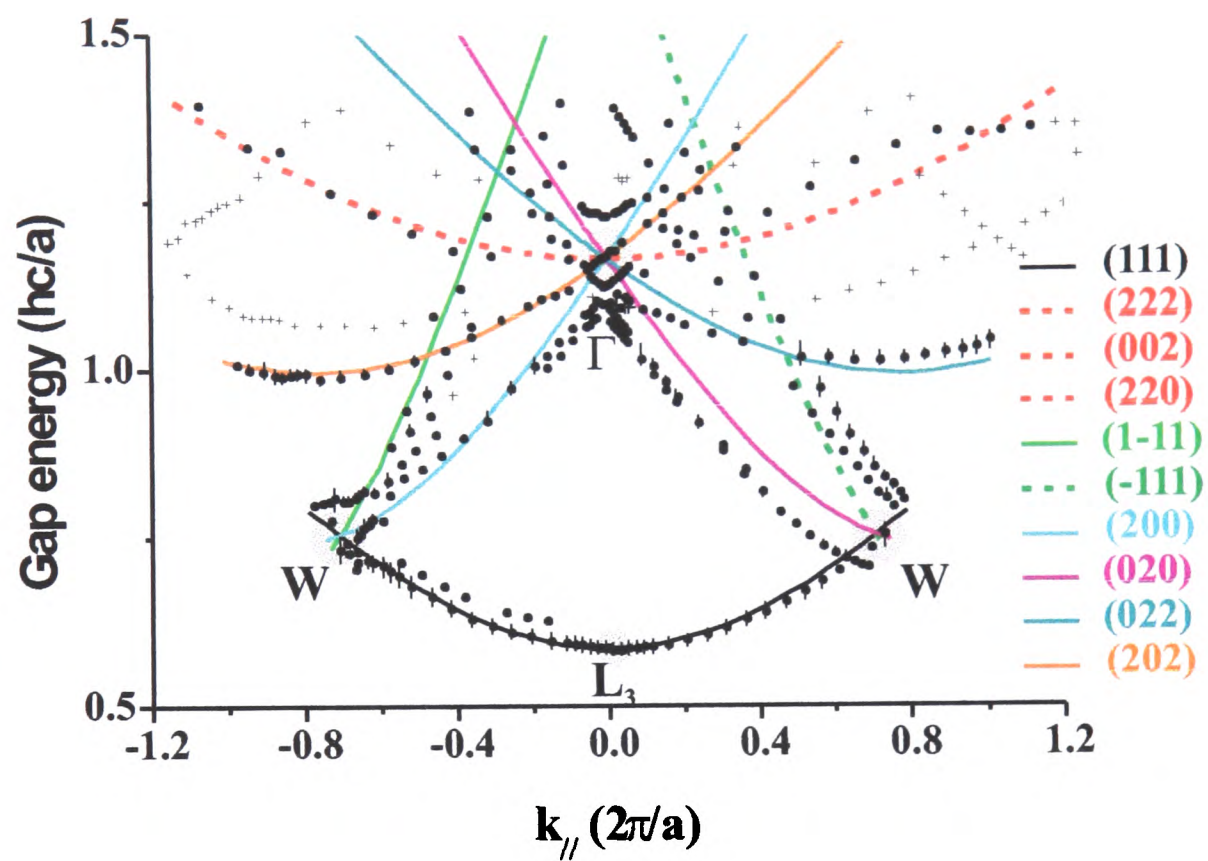


Figure 5.15: The minima in the transmission spectra (W-L₃-W scan) are plotted in units of energy versus $k_{||}$. The coloured lines show the Bragg scattering planes. The bars on the data show the full width at half minimum of the features. Dots represent features assigned to a Bragg scattering plane; crosses unassigned features.

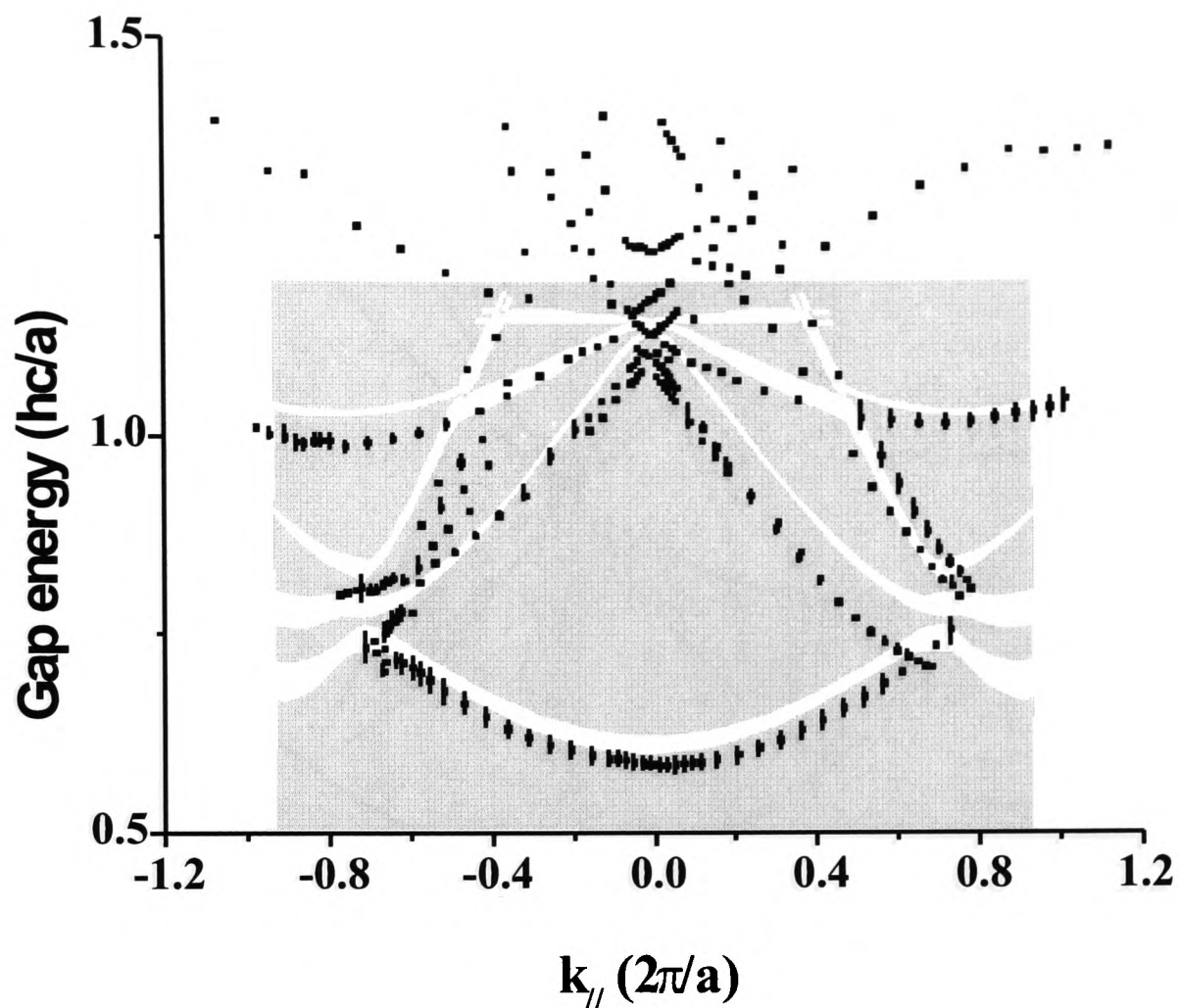


Figure 5.16: The minima in the transmission spectra (W-L₃-W scan) are plotted in units of energy versus $k_{||}$. Band edges, extracted from bandstructure, are also plotted for each bandgap. The bars on the data show the full width at half minimum of the features. Qualitatively, the width of the features agrees well with the band edges. The transmission minima identified in the Bragg scattering model match up well with the band edges. In this picture, we can view the transmission minima as the first bandgap, the second bandgap etc.

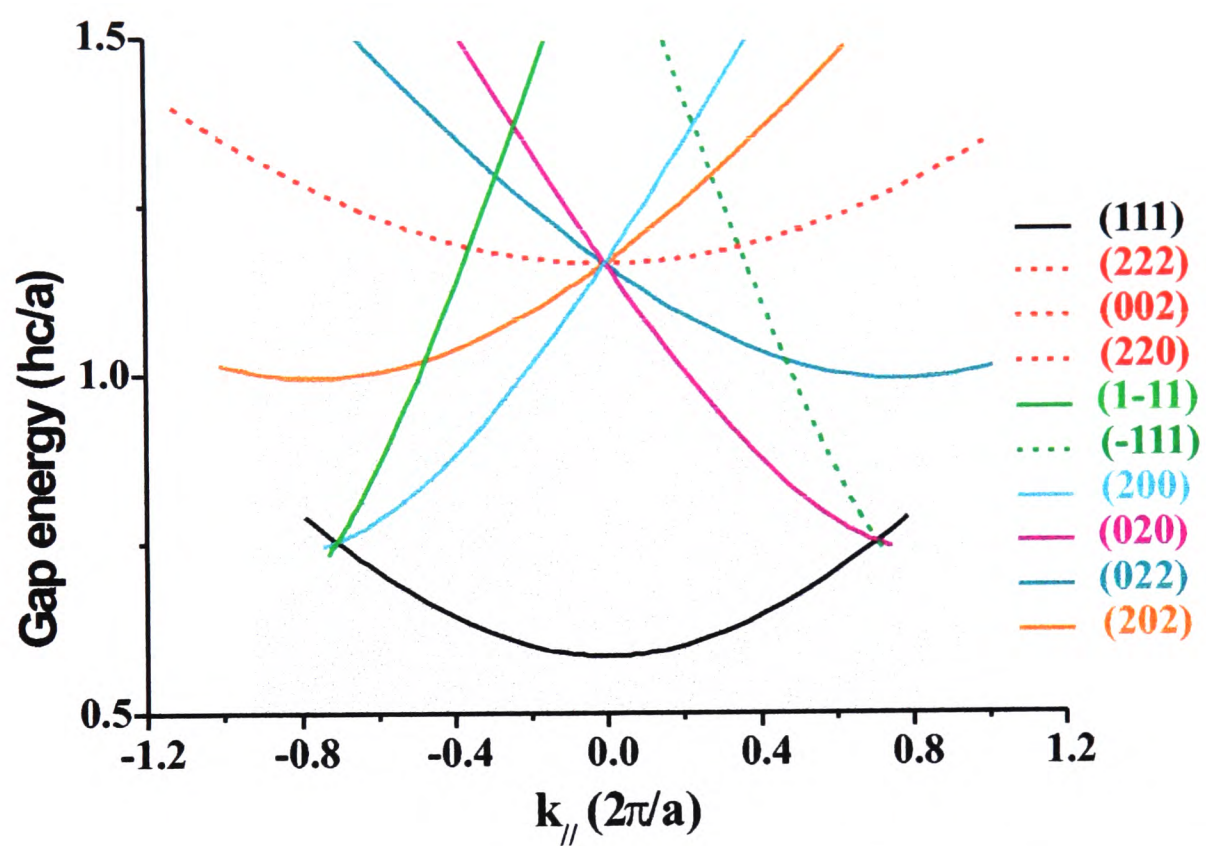


Figure 5.17: The Bragg scattering planes are plotted along with the band edges, extracted from bandstructure calculations for the W-L₃-W scan. The Bragg picture matches up well with the bandstructure picture for the low energy photonic bandgaps. The higher order bandgaps have lower energies than the Bragg scattering model suggests.

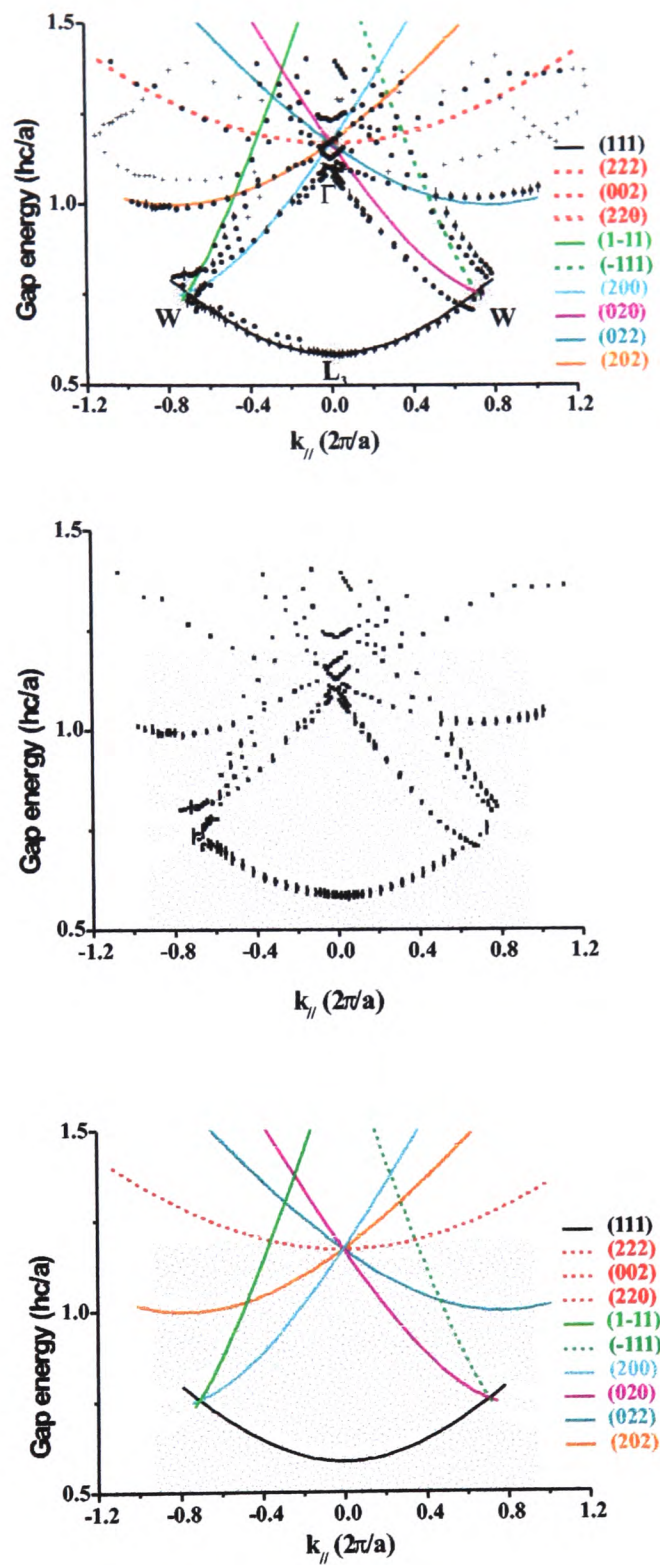


Figure 5.18: Composite figure, showing the transmission data fitted in a Bragg model, in a bandstructure picture and comparing the Bragg picture with the bandstructure picture for the W-L3-W scan.

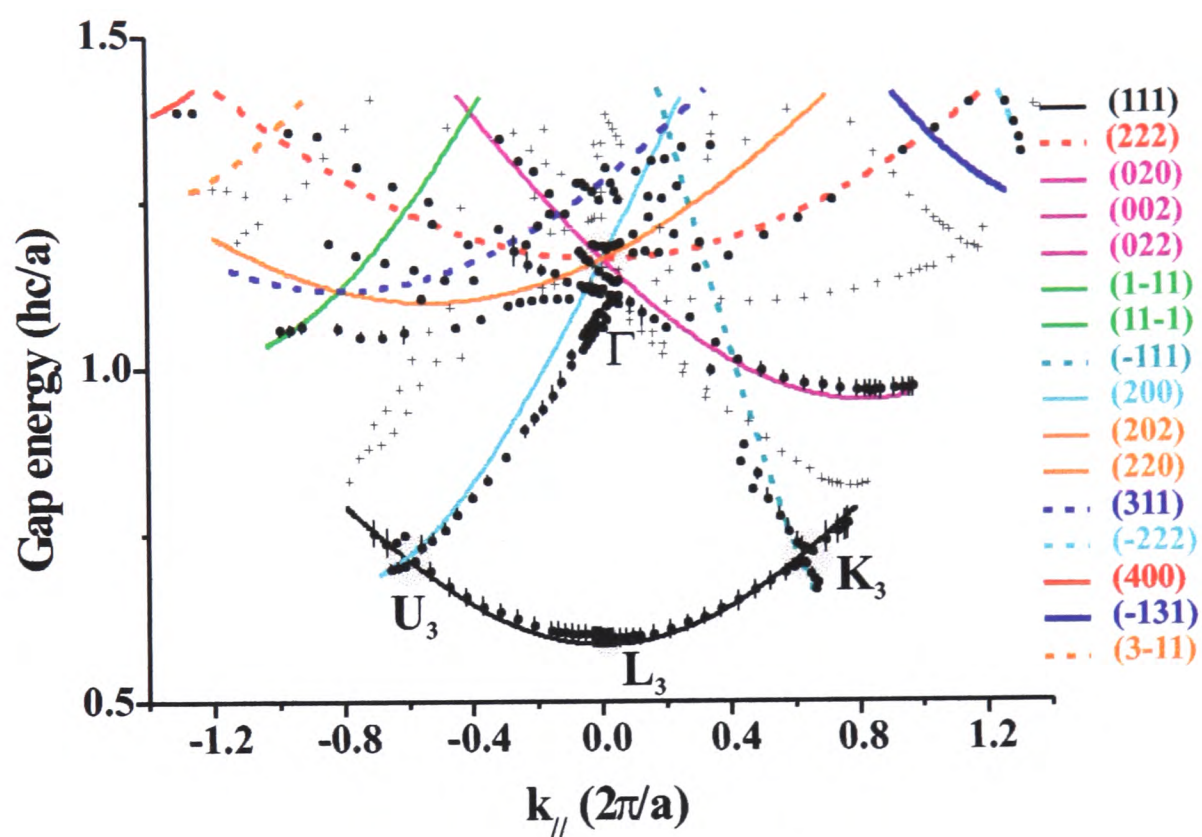


Figure 5.19: The minima in the transmission spectra (U_3 - L_3 - K_3 scan) are plotted in units of energy versus $k_{||}$. The coloured lines show the Bragg scattering planes. The bars on the data show the full width at half minimum of the features. Dots represent features assigned to a Bragg scattering plane; crosses unassigned features.

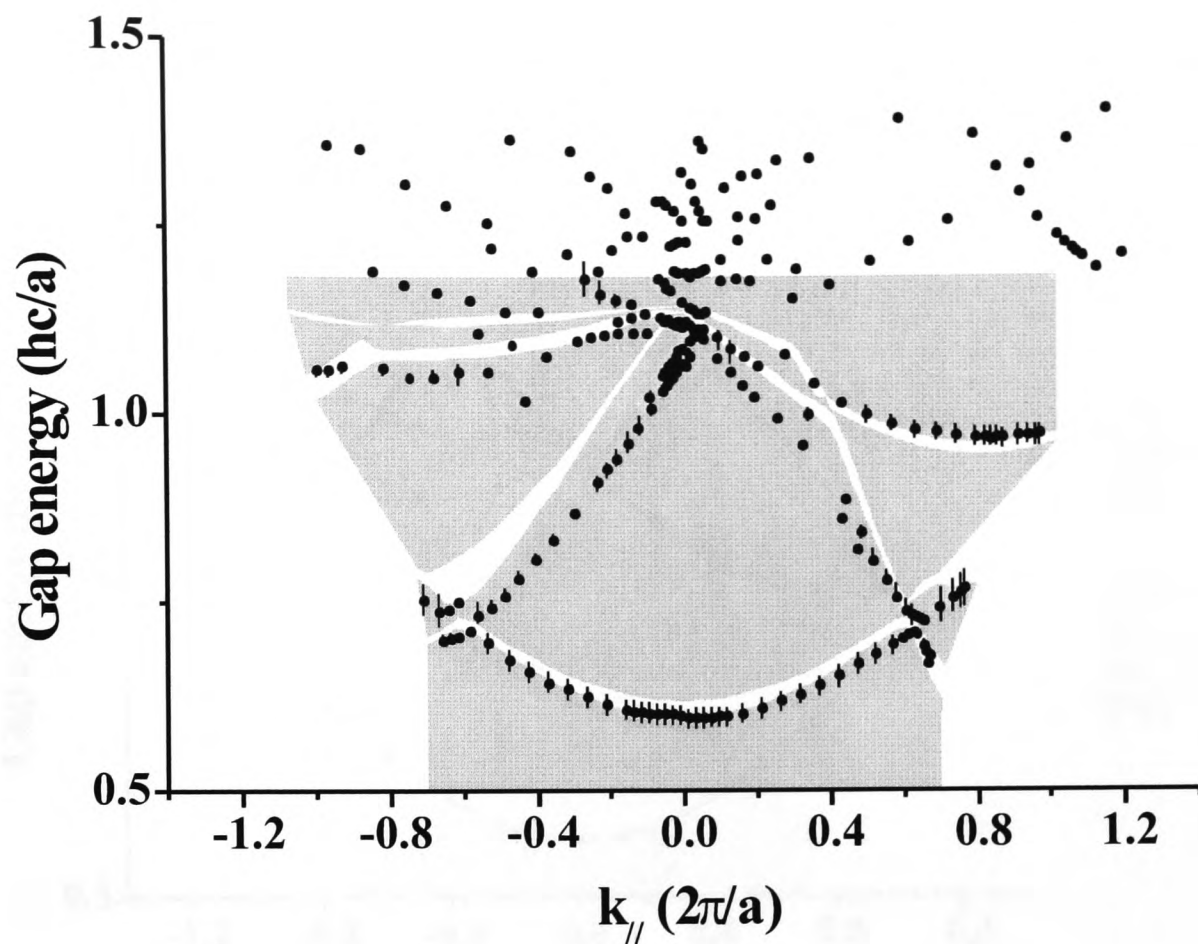


Figure 5.20: The minima in the transmission spectra (U_3 - L_3 - K_3 scan) are plotted in units of energy versus $k_{||}$. Band edges, extracted from bandstructure, are also plotted for each bandgap. The bars on the data show the full width at half minimum of the features. Qualitatively, the width of the features agrees well with the band edges. The transmission minima identified in the Bragg scattering model match up well with the band edges. In this picture, we can view the transmission minima as the first bandgap, the second bandgap etc.

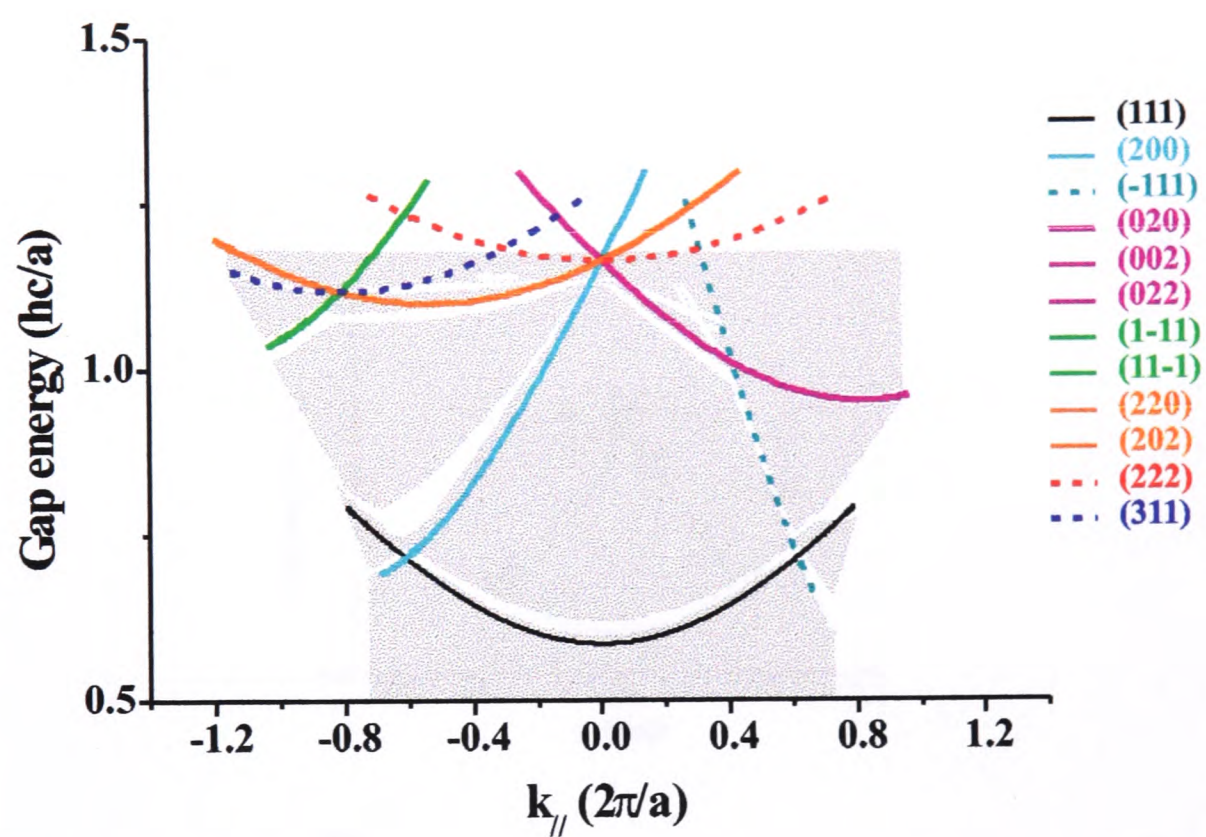


Figure 5.21: The Bragg scattering planes are plotted along with the band edges, extracted from bandstructure calculations for the U_3 - L_3 - K_3 . The Bragg picture overlaps well with the bandstructure picture for the low energy bandgaps. The third and fourth bandgaps however are lower in energy than the Bragg picture suggests.

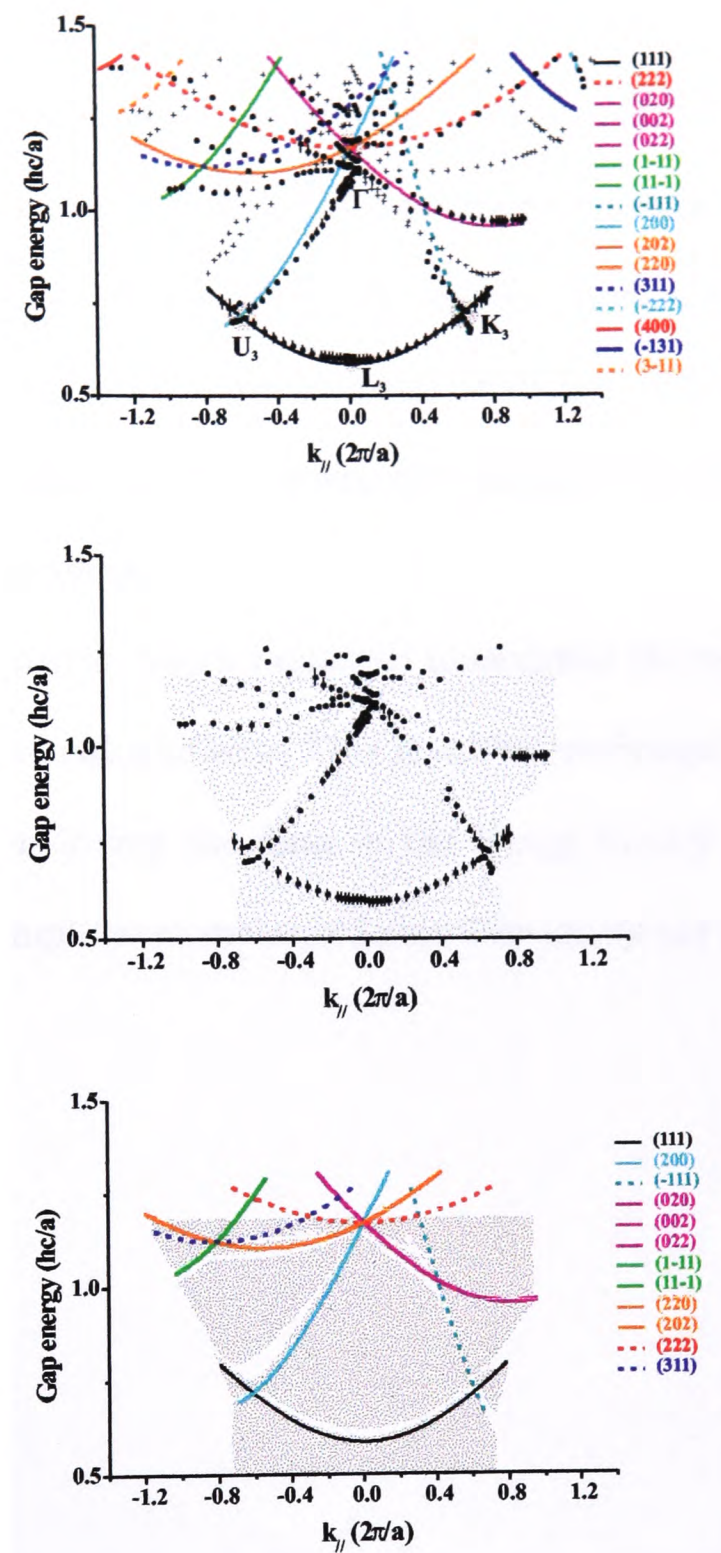


Figure 5.22: Composite figure, showing the transmission data fitted in a Bragg model, in a bandstructure picture and comparing the Bragg picture with the bandstructure picture for the U_3 - L_3 - K_3 scan.

being associated with the two polarisation eigenstates. Although the transmission data was polarised, the polarisation states do not necessarily correspond to polarisation eigenstates of the sample. When comparing the calculated band edges and the transmission data in figures 5.16 and 5.20, I have therefore not taken account of the polarisation eigenstates: when tracking the movement of the transmission minimum, I have plotted bands two and three, rather than one and three or two and four. Qualitatively, the measured width of the transmission gaps compares well with the difference between calculated bands: the measured width increases when the difference in energy between calculated bands increases and vice-versa.

The transmission features, which remained unassigned in the Bragg model, do not appear in the bandstructure calculations. This is useful confirmation that no interpretation errors were made when fitting the data in the Bragg model. It does however suggest that two areas of the sample were measured simultaneously (as discussed in section 5.4).

Chapter 6

397 nm Face-centred Cubic

Interference Pattern

In this chapter, I describe a photonic crystal structure fabricated using a face-centred cubic interference pattern with an ideal conventional lattice constant of $a = 397 \text{ nm}$ in air with an exposure wavelength of 355 nm . In section 6.1, I describe the interference pattern and briefly discuss our motivations for fabricating a photonic crystal with this pattern. In section 6.2, I describe the optical set-up required to generate this interference pattern. In section 6.3, I present some preliminary scanning electron micrographs of photonic crystals fabricated using the 397 nm face-centred cubic interference pattern.

6.1 ‘GaAs’ and ‘Diamond’ Interference Patterns

62 face-centred cubic interference patterns with a conventional lattice constant $< 3\mu\text{m}$ when the laser interference wavelength is 355 nm have been identified by Dr Sharp [79]. Of particular interest to us is the interference pattern with a conventional lattice constant of

397 nm in air with an interference wavelength of 355 nm [78]. The photonic bandstructure is shifted to shorter wavelengths than that for the 922 nm interference pattern due to the significantly smaller cube side. We expect that the fundamental gap, between bands two and three, to shift into the visible spectrum.

This pattern is of much interest to us for a variety of reasons. As I will show in section 6.1.3, a complete photonic bandgap opens up at a low refractive index contrast ($n = 1.87$ [79]). Structures with a complete photonic bandgap in the visible spectrum could have potential applications in, for example, integrated optics.

6.1.1 Wavevectors for the Face-centred Cubic Lattice

The wavevectors of the interfering beams determine the lattice, the beam polarisation vectors and relative beam intensities the basis geometry (c.f. chapter 3.1).

The wavevectors used to produce the face-centred cubic interference pattern with a conventional cube side of 397 nm in air, shown in figure 6.1, are the following:

$$\begin{aligned} \mathbf{k}_1 &= \pi/a [2 \ 0 \ 1] \\ \mathbf{k}_2 &= \pi/a [\bar{2} \ 0 \ 1] \\ \mathbf{k}_3 &= \pi/a [0 \ 2 \ \bar{1}] \\ \mathbf{k}_4 &= \pi/a [0 \ \bar{2} \ \bar{1}] \end{aligned} \tag{6.1}$$

As in the case of the 922 nm face-centred cubic interference pattern, the wavevector differences produce a body-centred cubic reciprocal lattice.

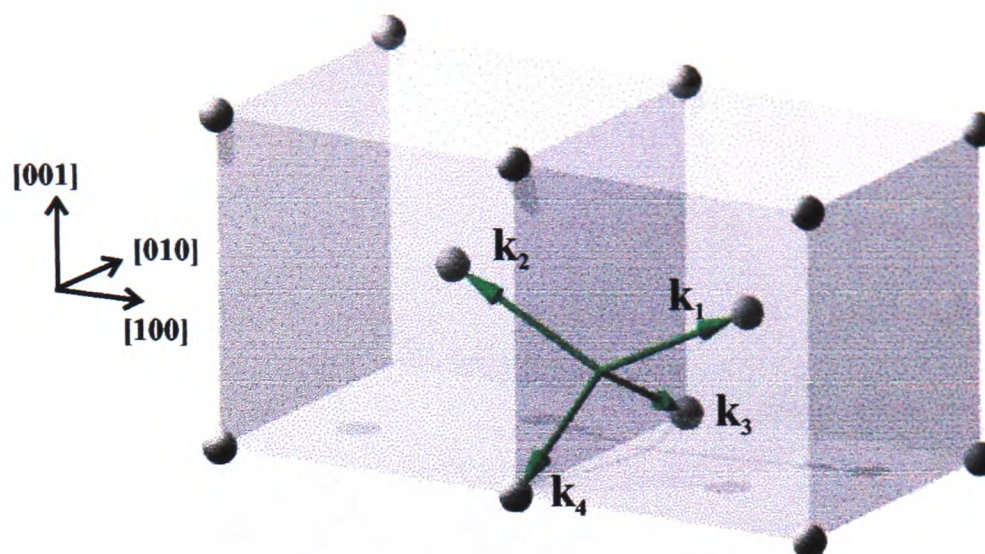


Figure 6.1: The beam geometry required to generate the 397 nm face-centred cubic interference pattern in air using a 355 nm exposure wavelength. In practice, the photoresist is exposed to the interference pattern in such a way that the (110) planes are parallel to the film surface.

6.1.2 Choice of Polarisations and Intensities

A symmetrical choice of elliptical polarisation vectors generates a basis with a ‘Gallium-Arsenide’ (GaAs) type geometry, which is more commonly known as the ‘zinc-blende’ structure. The ‘GaAs’ structure has the connectivity of a ‘diamond’ lattice, but each basis consists of two dissimilar ‘atoms’, one at $[000]$ and one at $a/4 [111]$, where a is the conventional cube side. One set of polarisation vectors, which generate this basis, are the following:

$$\begin{aligned}
 \mathbf{p}_1 &= [\bar{1} \sqrt{3} 2] + i [\bar{1} \sqrt{3} 2] \\
 \mathbf{p}_2 &= [1 \sqrt{3} 2] + i [1 \sqrt{3} 2] \\
 \mathbf{p}_3 &= [\sqrt{3} \bar{1} \bar{2}] + i [\sqrt{3} \bar{1} \bar{2}] \\
 \mathbf{p}_4 &= [\sqrt{3} 1 \bar{2}] + i [\sqrt{3} 1 \bar{2}]
 \end{aligned} \tag{6.2}$$

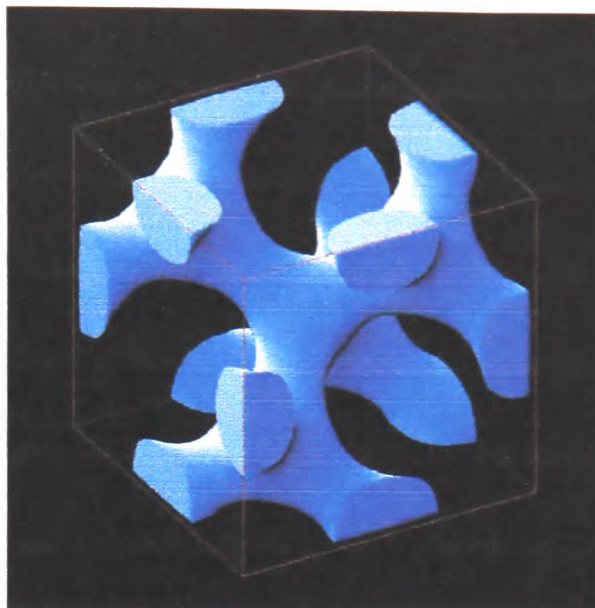


Figure 6.2: The isosurface shows a calculated constant intensity surface of the ‘GaAs’ interference pattern.

The intensities in the four beams are identical. Volume fill fractions ranging from 9% to 91% generate a ‘GaAs’ interference pattern consisting of a network of both three-dimensionally interconnected voids and material, which is necessary to ensure that solvent can penetrate into a structure fabricated with this pattern to dissolve unpolymerised material, leaving a robust three-dimensional structure. The intensity contrast in this interference pattern is infinite.

Figure 6.2 shows a calculated constant intensity surface of the face-centred cubic interference pattern with a conventional cube side of 397 nm with a ‘GaAs’ basis. One remarkable feature of this pattern is that the constant intensity surfaces at xI_{max} and $(1 - x)I_{max}$ map onto each other under a translation of $a/2$ along any of the cubic axes. So, for example, the ‘void’ volume at a threshold of $0.30I_{max}$ will map onto the ‘material’ volume at a threshold of $0.70I_{max}$. The isosurface also has no bottlenecks, which is a desirable attribute for fabrication, since it makes it easier for solvent to penetrate a crosslinked structure and clear out unpolymerised photoresist.

A less symmetric set of beam polarisation vectors have since been identified, which,

counterintuitively, generate a true ‘diamond’ basis [79]. These polarisation vectors are:

$$\begin{aligned}\mathbf{p}_1 &= \frac{1}{4\theta} ([\bar{1} \ 3 \ 2] + i\sqrt{3}[1 \ 1 \ \bar{2}]) \\ \mathbf{p}_2 &= \frac{1}{4\theta} ([1 \ 3 \ 2] + i\sqrt{3}[1 \ \bar{1} \ 2]) \\ \mathbf{p}_3 &= \frac{\theta}{4} ([0 \ 1 \ 2] + i\sqrt{3}[3 \ 0 \ 0]) \\ \mathbf{p}_4 &= \frac{\theta}{4} ([1 \ 0 \ 0] + i\sqrt{3}[0 \ \bar{1} \ 2])\end{aligned}\tag{6.3}$$

where $\theta = \sqrt[4]{\frac{4}{3}}$ gives maximum intensity contrast of 9.90. The beam intensities in all four interfering beams are identical. An alternative set of parameters have been proposed by [98]. These generate a low-contrast ‘diamond’ interference pattern, which is less practical to work with.

It is impossible to distinguish ‘GaAs’ and ‘diamond’ isosurfaces visually. To date, photonic crystals with the ‘GaAs’ interference pattern have been fabricated. The group plans to use the ‘diamond’ interference pattern in the near future.

6.1.3 Photonic Bandstructures for the ‘GaAs’ Pattern

I used the MIT Photonic-Bands code [14] to calculate the photonic bandstructures of photonic crystals with air-filled voids fabricated with the ‘GaAs’ interference pattern. Figure 6.3 shows that a complete photonic bandgap exists between the second and third bands for a refractive index contrast of $n = 2.25$ and a volume fill fraction of 50%. The midgap energy is ~ 0.58 , which corresponds to a wavelength of $397/2.25/0.58 = \sim 300 \text{ nm}$, in the UV.

If the photonic energy gap to mid-gap ratio between energy bands two and three, defined in equation 4.3, is positive, then a complete photonic bandgap has opened up. A systematic search of the gap to mid-gap ratio as a function of volume fill fraction at

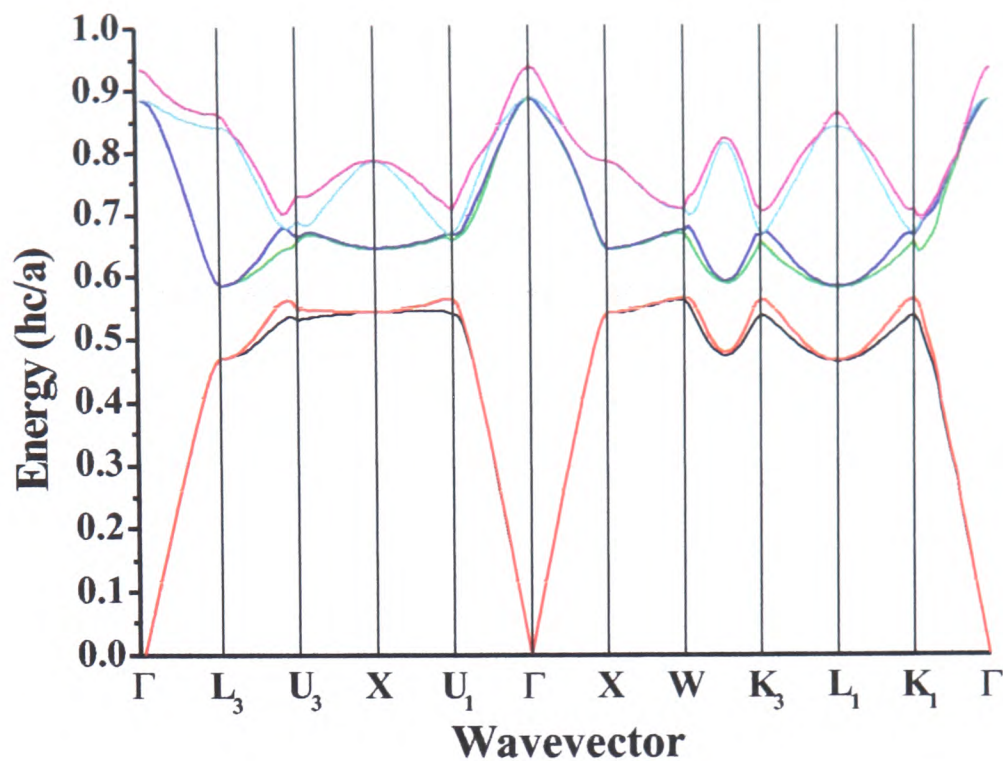


Figure 6.3: A complete photonic bandgap exists between the second and third bands in a structure exposed to the ‘GaAs’ interference pattern for a refractive index contrast of 2.25 and a volume fill fraction of 50%.

different refractive index contrasts, plotted in figure 6.4, shows that a complete bandgap first opens up for a refractive index contrast of 1.90 and a volume dielectric fill fraction ranging between 30% and 40% material to void.

The difference in photonic band energies of the ‘diamond’ structure and the ‘GaAs’ structure is too small to be distinguishable on any graphs in this thesis.

6.2 Practical Implementation of the 397 nm Face-centred Cubic Pattern

I designed and built the optical holographic set-up to generate the face-centred cubic interference pattern with a conventional cube side of 397 nm. In the interference pattern with a 922 nm conventional cube side, the four wavevectors are incident from the same

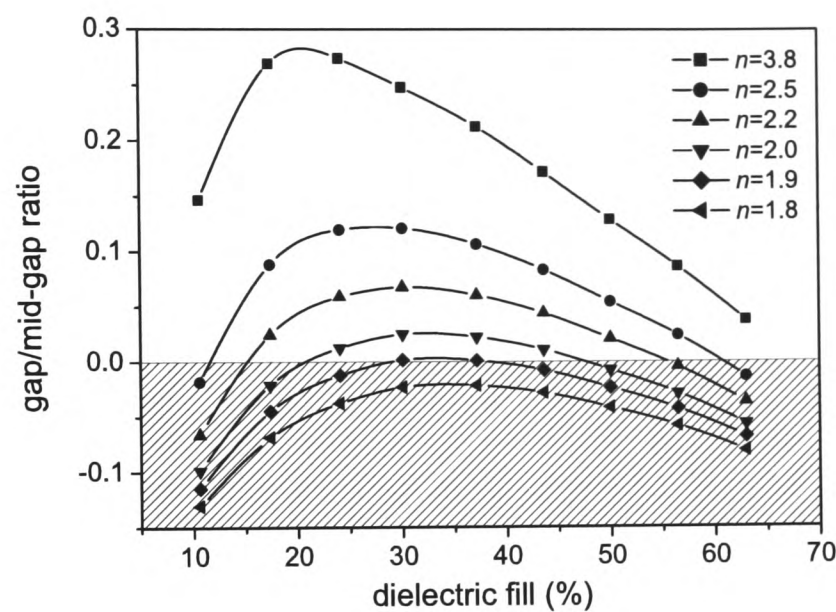


Figure 6.4: The photonic energy gap to mid-gap ratio for the second and third photonic bands is plotted as a function of volume fill fraction for the ‘GaAs’ interference pattern. Each curve represents one refractive index contrast. A positive gap to mid-gap ratio implies that a complete three-dimensional photonic bandgap has opened up; a negative ratio implies that the energy gap between the second and third bands does not overlap in all directions in reciprocal space. A complete band gap first opens up for the ‘GaAs’ structure at a refractive index contrast of 1.90 and a fill fraction between 30% and 40% material to void.

half-space; this makes the pattern relatively easy to implement in practice. In the pattern with a 397 nm cube side however, two beams are incident from one half-space, two beams from the other half-space. It is therefore particularly important to design the opto-mechanical hardware with laser safety concerns as a first priority as there will be laser beams directed up from as well as down towards the optical table.

For reasons which will become clear further on, I have chosen to pair the wavevectors $\mathbf{k}_1$ and $\mathbf{k}_3$, directing the laser beams corresponding to these wavevectors down onto the optical table, and the wavevectors $\mathbf{k}_2$ and $\mathbf{k}_4$, with the laser beams corresponding to these laser beams directed up from the optical table. A fused silica substrate, spin-coated with the photoresist, is placed at the intersection of the four beams. In this orientation, the photoresist is exposed with the (110) planes parallel to the film surface. For safety reasons, I image the intersection region with a CCD camera and view a target at the intersection on screen whilst lining up the beams to prevent any scattered or stray beams from causing injury.

I use the epoxy-based polymer SU-8 with a triaryl sulfonium salt as the photoresist and the processing techniques described in section 3.5, which were developed for the fabrication of photonic crystals using the interference pattern with a 922 nm cube side. The advantage of using this material system is that I have much experience of working with it. Identifying a suitable alternative and developing the necessary processing steps could take several years. The disadvantage of using SU-8 is that it may not have the required resolution to reproduce the sub-0.1 μm features of the optical lattice accurately. It is capable of sub-0.1 μm resolution, but it is unclear whether SU-8 is capable of such high resolution in three dimensions, over a large volume. Features as small as 50 nm across have been produced in SU-8 in one dimension, but these features tend to be many

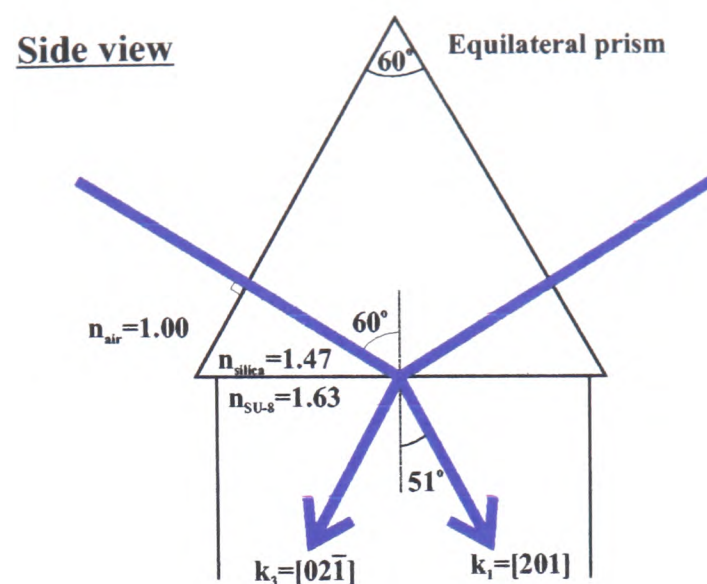


Figure 6.5: The side view shows how the wavevectors are refracted through an equilateral prism made of fused silica to generate a face-centred cubic interference pattern inside the thin film of photoresist (SU-8).

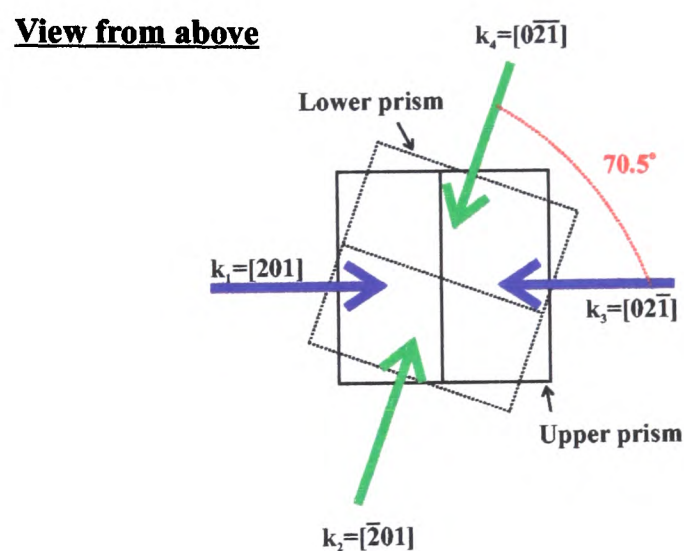


Figure 6.6: We use two equilateral prisms with the photoresist spin-coated onto a substrate, which is sandwiched between the two prisms. The prisms are rotated with respect to each other by an angle of 70° about an axis passing through the centre of their apices. k_1 and k_3 are refracted down through the upper prism (solid outline) into the photoresist, k_2 and k_4 refracted up through the lower prism (dotted outline) into the photoresist.

hundreds of microns in size in the other two dimensions [99].

It is impossible to refract the beams directly into the photoresist as the angles required to generate a face-centred cubic lattice inside the resist are greater than the critical angle of SU-8, so the beams are refracted into the resist through prisms.

I use two equilateral prisms made of UV-grade fused silica with a refractive index of 1.47 at an exposure wavelength of 355 nm, as shown in figure 6.5. The film is spun onto the standard fused silica disk, and the disk and the two prisms are sandwiched together with an index-matching mineral oil (refractive index 1.467 at 355 nm), as described in chapter 4.3. The two prisms are rotated by 70.5° with respect to each other about an axis passing through the centre of the two apices, as shown in figure 6.6. The beams are normally incident onto the prism facets. The beams are incident at an angle of 60° at the prism-film interface; they are refracted into the photoresist to form a face-centred cubic lattice inside the resist. By choosing to refract the wavevectors $\mathbf{k}_1$ and $\mathbf{k}_3$ through the top prism and $\mathbf{k}_2$ and $\mathbf{k}_4$ through the lower prism, it is a relatively simple task to generate a face-centred cubic lattice inside the photoresist using standard optics. One point to note is that $\mathbf{k}_2$ and $\mathbf{k}_4$ travel through the thickness of the silica substrate ($\sim 2\text{ mm}$) and cross one extra interface at the fused silica-fused silica boundary between the prism and the substrate before reaching the target. Since these materials are approximately optically matched and the additional optical path length is small, no problems should arise.

6.3 Scanning Electron Micrographs

In this section, I present some scanning electron micrographs of the first photonic crystals fabricated in SU-8 using the ‘GaAs’ interference pattern with a conventional cube side of 397 nm in air. The electron micrographs show that there is regular structure in the

samples. The photoresist is exposed to the interference pattern with the (110) planes parallel to the film surface.

The conventional cube side of the interference pattern in SU-8 is only $397/1.63 = 244 \text{ nm}$. Figure 6.7 shows the arrangement of the ‘atoms’ in a conventional cube for a diamond structure. The bonds are shown in red; the (110) plane is shaded and the ‘atoms’ lying in the (110) plane have been coloured blue. The connectivity and spacings remain the same for a GaAs structure. The spacings between ‘atoms’ lying in the (110) plane are shown in figure 6.8. We expect to see sub- $0.1 \mu\text{m}$ features in any SU-8 photonic crystals exposed with the ‘GaAs’ interference pattern.

Imaging such structures is difficult. Sputter-coating the photonic crystal with gold, which is necessary for imaging the structures in the electron microscope we normally use (JEOL JSM 6300), imposes a limit on the minimum resolvable feature size. The photonic crystals fabricated with the ‘GaAs’ interference pattern cannot be imaged in the JSM6300 microscope using our established routine described in section 3.4. We therefore adopted a new sputter-coating protocol and used a higher resolution scanning electron microscope, the JEOL JSM-6500F, to image our photonic crystals. Minimum spatial resolution is 3 nm , achievable at low voltages, which prevents our samples from charging up.

Figure 6.9 shows a calculated constant intensity surface of the interference pattern with the (110) plane parallel to the front surface. A scanning electron micrograph, shown in figure 6.10, enables us to compare the calculated isosurface with the photonic crystal surface. The patterning of the (110) surface in the structure is remarkably similar to the isosurface (110) plane. This is evidence that the photonic crystals have the expected ‘GaAs’ symmetry.

Figure 6.11 shows a scanning electron micrograph of the top surface of a photonic

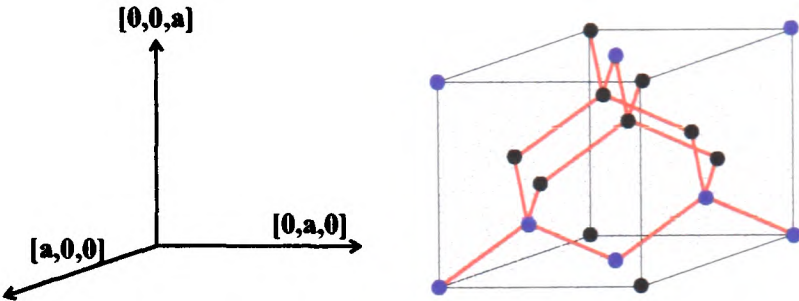


Figure 6.7: The schematic shows the distribution of the ‘atoms’ in a conventional cube for a diamond lattice. The red lines show the diamond connectivity. ‘Atoms’ in the (110) plane are marked in blue. The (110) plane is shaded grey.

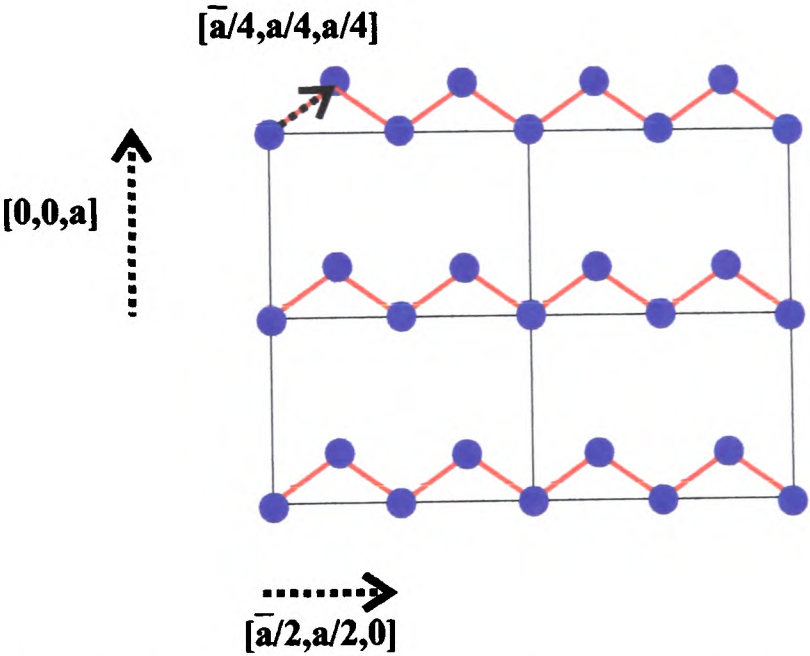


Figure 6.8: This diagram shows the spacing of the ‘atoms’ in the (110) plane of the ‘GaAs’ interference pattern. The bonds between ‘atoms’ are shown in red.

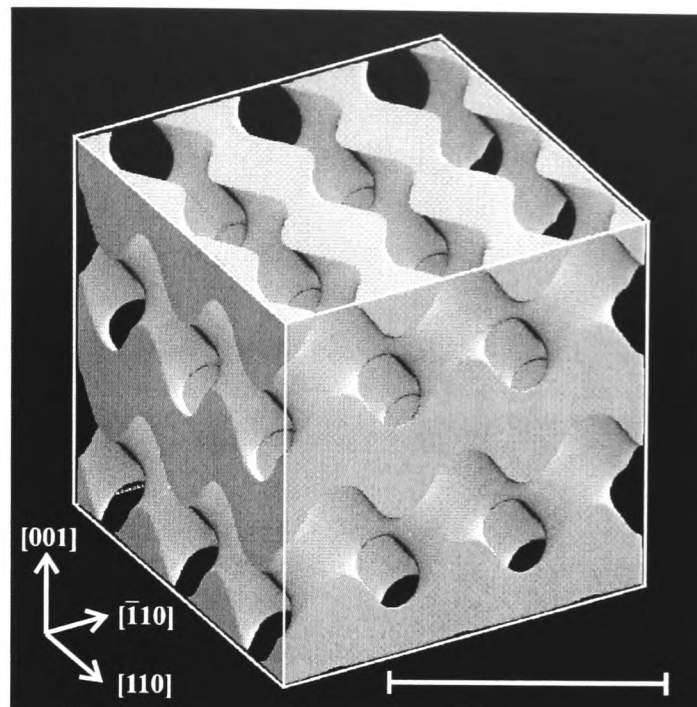


Figure 6.9: The calculated isosurface generated with the ‘GaAs’ beam configuration is orientated with the (110) plane parallel to the surface. The scale bar shows the conventional lattice constant.

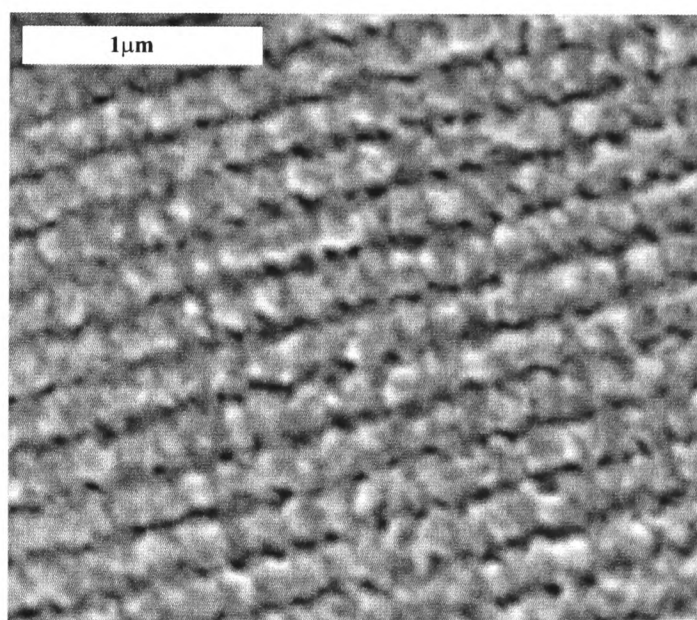


Figure 6.10: The scanning electron micrograph shows the top surface, (110) plane, of a photonic crystal in SU-8, fabricated with the ‘GaAs’ face-centred cubic interference pattern with a conventional lattice constant in air of 397 nm. The ‘atoms’ are arranged in the regular pattern expected from the isosurface in 6.9.

crystal, which was exposed with the ‘GaAs’ interference pattern. Although the micrograph is a little blurred, it is possible to see that there is regular patterning on the top surface. A Fast Fourier Transform of the image, shown in figure 6.12, confirms that the structure is periodic. By measuring the spacing between the diffraction spots, we can determine the average spacing between ‘atoms’ lying in the (110) plane. These are $\alpha = |[0\ 0\ a]| = 200\text{ nm}$, $\beta = |[\bar{a}/2\ \bar{a}/2\ 0]| = 140\text{ nm}$ and $\gamma = |[a/4\ a/4\ a/4]| = 111\text{ nm}$, where $a = 244\text{ nm}$ is the conventional cube side of the interference pattern in SU-8. This implies that polymerisation initiated shrinkage is inhomogeneous in the (110) plane. Along $[0\ 0\ 1]$ and $[\bar{1}/2\ \bar{1}/2\ 0]$, the polymerised structure shrinks to $200/244 = 81\%$ of the interference pattern, but along $[1/4\ 1/4\ 1/4]$, shrinkage is $111/106 = 105\%$, i.e. the structure actually expands in this direction. As a result, the structure is slightly distorted compared to the interference pattern. This inhomogeneous shrinkage will need to be counteracted in some way before photonic crystals with a genuine ‘GaAs’ structure can be produced.

To date, there are no scanning electron micrographs of cleavage planes through the ‘GaAs’ photonic crystals, so it is unclear if the photonic crystals have a periodic structure through their entire depth. It is conceivable that due to the very small ‘interatomic’ spacings, the structure is overpolymerised, and unpolymerised SU-8 has not cleared out properly in the bulk of the crystal. This will need investigating before we can be confident that our current photoresist formulation is suitable for fabricating these microstructures.

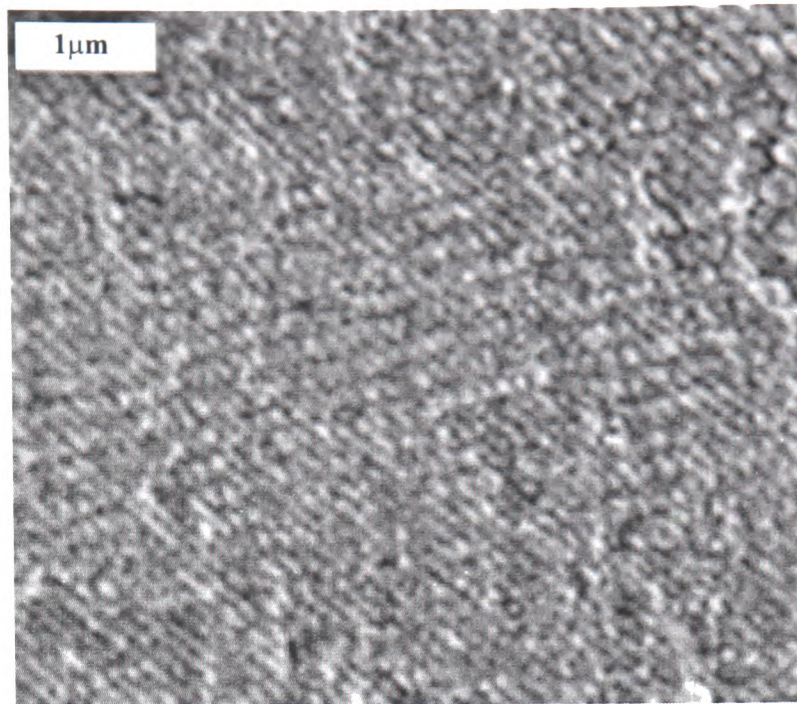


Figure 6.11: The scanning electron micrograph shows the top surface, (110) plane, of a photonic crystal, fabricated with the ‘GaAs’ face-centred cubic interference pattern.

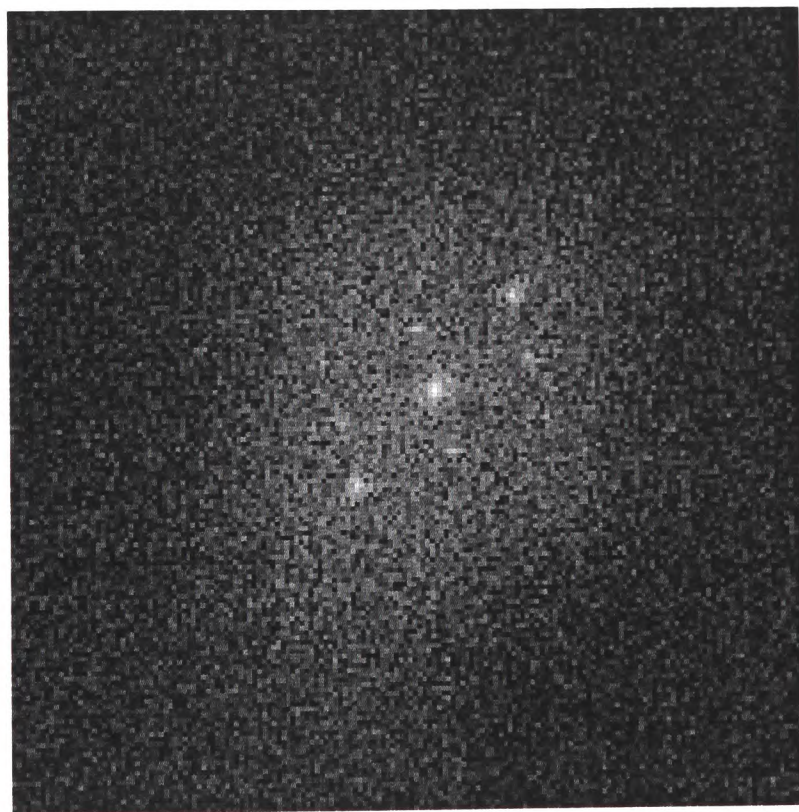


Figure 6.12: The diffraction spots in the Fast Fourier Transform of the micrograph in figure 6.11 show that the structure is periodic.

Chapter 7

Conclusion

Photonic crystals show much promise for future photonic technologies. An ever-increasing number of groups are researching photonic crystal properties, devising new techniques for fabricating photonic crystals and including targeted defects with the aim of eventually producing marketable devices. If the full potential of photonic bandgap materials is to be realised, then it is essential that a flexible technique for fabricating three-dimensional photonic crystals with a complete photonic bandgap and deliberately engineered defects is developed.

We believe that holographic lithography is such a technique: it is flexible, quick and comparatively cheap to produce structures with periodicity over many hundreds of units cells; reproducibility is good. We have demonstrated that the polymeric crystals can serve as templates for fabricating high refractive index contrast photonic crystals, which we calculate will have a complete photonic bandgap. First developed in our group [9], several other groups have realised the potential of holographic lithography [69, 98]. Our group is currently developing methods for introducing defects into the crystal, which are commensurate with the lattice, and has already written waveguides in photonic crystals

with a 922 nm conventional cube side.

In this thesis, I have concentrated on two lattice geometries, a face-centred cubic lattice with a conventional cube side of 922 nm and a ‘GaAs’ geometry with a conventional cube side of 397 nm in air. I have used both interference patterns to fabricate photonic crystals in SU-8. Scanning electron micrographs of these photonic crystals show that they match up remarkably well with calculated isosurfaces of the generating interference patterns. Optical transmission measurements demonstrate that the structures have well-defined, narrow and deep transmission gaps. These gaps do not overlap in frequency; the photonic crystals cannot have a complete photonic bandgap since their refractive index contrast is too low.

Defect-writing in our photonic crystals is currently being developed by several colleagues. An acid-sensitive dye is added to the photoresist in order to image the lattice of protons, after exposure and before polymerisation, in a confocal microscope. The confocal microscope allows them to image the proton lattice and write the defects simultaneously. The ‘GaAs’ pattern is also being developed further. The processing parameters need to be fine-tuned for this interference pattern, and a new photoresist might need to be introduced. There is also the possibility of generating the ‘GaAs’ interference pattern with the fundamental Nd:YAG wavelength, 1064 nm, which would lead to a conventional cube side of 1191 nm in air. Photonic crystals fabricated with this pattern could be engineered to have a complete photonic bandgap in the telecommunications wavelength range ($\sim 1.2\text{--}1.5\ \mu\text{m}$). Finally, the group is developing a templating program to fabricate photonic crystals in high-index materials with the aim of producing complete photonic bandgaps.

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