Low Threshold Organic and Quantum Dot Nanobeam Lasers

by

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Submitted to the Department of Electrical Engineering and Computer Science
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Abstract

Lasers in the visible spectrum have many applications including sensing, medical, and entertainment applications. Traditional semiconductors face challenges that limit their ability to create lasers for the visible spectrum. Organic materials and quantum dots are an attractive alternative for visible lasers due to their broad, tunable emission and deposition using fabrication techniques of low complexity. These materials have been used to demonstrate low lasing thresholds, and we hope to improve upon them with a novel design, paving the way towards electrically pumped and continuous wave operation lasing.

In this thesis we couple the use of organic materials and quantum dots with one dimensional nanobeam photonic crystal cavities to design lasers for the visible spectrum. We cover the theory behind generation of optical gain and lasing as well as the theory of photonic crystals. We outline a strategy for designing laser cavities using the chosen gain materials. Finally, we demonstrate a low lasing threshold of 4.2 μJ/cm² for our organic lasers.

Thesis Supervisor: Vladimir Bulović
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The y component of the electric field for the cavity mode is plotted.

The fabrication of an organic laser.

The overexposure of HSQ is evident from the filled in holes in the photonic crystal.

SEM images show the effect of annealing on devices. In (a) we see that without annealing, many of the devices are broken, and in (b) a device that has been annealed was successfully fabricated.

SEM images show a completed device, after evaporation of organics, both (a) from a tilted view and (b) from the top. We see that the holes are open in the organic layer, forming a photonic crystal cavity.

The samples are characterized by the setup shown. Input pulses are expanded and clipped to achieve a flat intensity profile. The pump laser light is spectrally filtered from the collected laser light. The device emission is analyzed on a spectrometer.

Through optical characterization of our devices, we see the signatures of lasing. (a) We see a characteristic threshold in the intensity as a function of input absorbed energy density. We also see linewidth narrowing of the lasing mode, down to the limit of our spectrometer. (b) We observe lasing through a distinct cavity mode.

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Chapter 1

Introduction

Light has been a subject of great interest to scientists since the early origins of humanity. According to historians, the Greek philosopher Eratosthenes is said to have estimated the size of the Earth by comparing the lengths of the shadows cast by objects illuminated by the sun in Alexandria and Syene. Though our methods have become more sophisticated since then, we still rely on the precise manipulation of light for the purposes of great scientific and technological importance.

One of the most important light sources we have is the laser, and this claim is well illustrated by the large market for lasers that brought in more than $8 billion in 2013 for a variety of applications[1], shown in Figure 1-1. The long intercontinental networks that form the backbone of the internet rely on lasers to encode data into packets of light sent over hundreds of kilometers through optical fibers with low loss. Lasers have even demonstrated communication with the moon at speeds six times faster than current state of the art radio communications[4]. The optical storage market uses lasers for reading and writing disc media and other storage devices. Lasers are also used in the material processing industry for cutting, welding, and drilling of metals and for various purposes in semiconductor processing including lithography. Finally, lasers are an important spectroscopic tool used for sensing and imaging because of their ability to deliver controlled packets of light over precise regions in both time and space.

The market for lasers has continued to grow over the past decade despite the global
Figure 1-1: **Top:** Laser revenue over the past 30 years; **Bottom:** Breakdown of 2013 laser revenue by application[1]

economic recession of 2008. Conventional semiconductor diode lasers still comprise about half of the total laser sales, but the laser market for the largest 2 markets, telecommunications and optical storage, has seen its growth rate slow since 2011, speculated to be due to smartphone saturation and hesitation of communications service providers to upgrade their networks. The medical, instrumentation and sensing, and entertainment and display markets, however, are seeing rapid growth[1] (see Figure 1-2). In these emerging markets, visible wavelength lasers are particularly important.

Conventional semiconductor lasers have a limited ability to cover the visible spectrum. The aluminum gallium indium phosphide (AlGaInP) family of semiconductor...
Revenues ($M)
Year 2009 2010 2011 2012 2013
(a) Telecom and Optical Storage
3154 3636 3671 3883 3636
3270 330 356 389 3154
(b) Medical
205 2591 441 476 503 532
(c) Instrumentation and Sensing
77 84 116 165 213
(d) Entertainment and Displays

Figure 1-2: Laser revenue by application. Although the telecom and optical storage market has seen a reduction in growth, the medical, instrumentation and sensing, and entertainment and display markets continue to see aggressive growth[1]

Alloys, commonly used for infrared lasers, does not contain lattice-matched alloys with bandgaps higher than around 2.36 eV [2] (see Figure 1-3). Devices operating near this limit have shallow quantum wells, limiting their ability to confine charge carriers. Therefore, the AlGaInP family cannot create lasers that span the entire visible spectrum.

Figure 1-3: The energy gap for the AlGaInP family is shown, with the dotted line representing the alloys that are lattice matched with GaAs. We see that the largest value bandgap along this line is 2.36 eV[2].

The alloys of the aluminum gallium indium nitride (AlGaN) family cover the
entire visible spectrum, but face different challenges for making lasers. To grow a laser with green emission, the alloy requires a high indium fraction\cite{5}. Due to the high mismatch in the lattice parameter\cite{6}, the growth of the crystal must be along the c-plane of the GaN substrate\cite{5}. The problem is that after annealing these alloys at high temperatures, a process that is commonly used to remove defects from the lattice, in this configuration, indium atoms are found clustered together forming pockets \cite{7}. These nonuniformities in the crystal lattice degrade device performance. Because of these challenges, the AlGaInN family, too, is limited in its coverage of the visible spectrum.

1.1 Organics and Quantum Dots

Organic molecules are an alternative to traditional semiconductors that have been successfully integrated into lasers for the visible spectrum. Since their invention in the 1960s, lasers employing liquid solutions of organic laser dyes have been used for various applications. Laser dyes emit light throughout the visible spectrum, and the broadband emission of each individual dye makes them suitable for use in tunable lasers. The downside to these lasers are that they require bulky pumps to circulate the laser dye solution, and the dyes photobleach with time, reducing laser output power, and must be replaced.

The demonstration of solid state lasing in thin films of organic molecules\cite{8, 9} has sparked interest in using organic semiconductors as for creating more compact visible lasers. In addition to the broad range of tunability offered by laser dyes, organic semiconductor molecules have other advantages for lasers, including fabrication methods. Organic molecules can be deposited over large areas using low complexity fabrication techniques. Thin films of small molecules can be thermally evaporated onto virtually any substrate without the constraint of lattice matching or the requirement of ultra-high vacuum necessary for materials grown by epitaxy. Larger molecules, like polymers can be spin coated or drop cast onto substrates as well, and the thickness of the films can be controlled by surface treatments of the substrate and by varying
Despite the advantages offered by organic molecules for lasers, there are several drawbacks that have hindered their implementation for electrically pumped and continuous wave (CW) operation lasers. The largest problem for these two applications is the presence of long-lived "dark" triplet energy levels in the excited state. These triplet states have zero dipole transition probability for radiative recombination in the absence of perturbations, and the population of these states negatively impacts the quantum efficiency. Organic molecules also have low charge carrier mobility, due to the strong localization of carrier wavefunctions, and tend to photo-oxidize in air environments. While researchers have been working to overcome these challenges, others have looked to new material systems that offer similar advantages as organic molecules, such as tunability and solution processability, without sharing these drawbacks.

Semiconductor nanocrystals, commonly referred to as quantum dots (QDs), are another material system that offers a tunability over a large spectrum. Colloidal quantum dots, are quantum dots grown in solution instead of by epitaxy, and this allows for finer control over the size distribution of QDs as well as solution processability[10]. The size of the quantum dots is important. By changing the radius of these quantum dots, we can control their energy levels, and therefore tune their emission and absorption spectra, which is shown in Figure 1-4. Reducing the size of dots increases the confinement of excited states, which increases their energy and blueshifts their absorption and emission spectra. Furthermore, by functionalizing the surface of these dots with organic ligands, quantum dots show a dramatically improved photostable in the presence of air when compared with organics. Finally, the implementation of a core-shell dot structure has largely eliminated the problem of triplet-like dark states, with the internal quantum efficiency of these QDs reaching 90% [11]. Multicolor lasing using single exciton gain has recently been demonstrated in colloidal quantum dots[3], although at threshold energies $\sim100\times$ larger than that of organics. There remains much room for improvement for QD lasers in lowering their threshold.
All lasers require 3 common elements, a pump, a gain material, and a cavity. We have thus far introduced the idea of using organic molecules and quantum dots as gain materials, and have considered optical pumping only, as electrically pumped lasing has eluded researchers working with these materials. Before we can talk about cavities, and large role they play for lasers, we need to take a step back and consider the lasing threshold condition. We know from the literature that the following condition holds for lasers[12]:

\[ N_{th} \propto \frac{V_{eff}}{Q} \]  

(1.1)

where \( N_{th} \) is the threshold density of excited states, \( V_{eff} \) is the mode volume of the lasing mode, and \( Q \) is the quality factor of the lasing mode. Clearly, to lower the lasing threshold, we want to design a cavity with a high quality factor that simultaneously minimizes the mode volume. We also want to limit the number of modes if possible. Equation 1.1 holds true for every lasing mode and each mode will deplete the population of excited states. Every lasing mode will have to compete with each other, so it is best to try to design a cavity that supports only a single mode.

Table 1.1 shows a comparison between some of the most common configurations of optical cavities. Clearly there is a trade-off for most cavities between increasing the
quality factor, and decreasing the mode volume. The class of cavities that perhaps seems the most promising for lowering the threshold of lasers is the one dimensional photonic crystal. These structures are often called nanobeam photonic crystal cavities in the literature, due to their waveguide or beam-like geometry. In addition to their high $Q/V_{eff}$ ratios, nanobeam photonic crystal cavity’s offer other unique advantages with respect to fabrication techniques that we will discuss later.

Table 1.1: Commonly used optical cavities are compared by two figures of merit, $Q$ the quality factor and $V_{eff}$ the mode volume. Note that quantities surrounded by parentheses are calculated values, instead of reported values. See the associated footnotes for details on the calculations.

<table>
<thead>
<tr>
<th></th>
<th>Fabry-Perot</th>
<th>Whispering Gallery</th>
<th>Photonic Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda[12]$</td>
<td>Extended$[13]$</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>$10^3$</td>
<td>$(2 \times 10^6)^1$</td>
<td></td>
</tr>
<tr>
<td>$V_{eff}$ $\left(\left(\frac{\lambda}{n}\right)^3\right)$</td>
<td>5</td>
<td>$(128)^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(\sim 12,000)^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0096</td>
<td>1.2</td>
</tr>
</tbody>
</table>

1.3 Thesis Outline

In this thesis we investigate the use of organic molecules and quantum dots as gain materials for a laser that utilizes a nanobeam photonic crystal cavity. We first introduce the underlying physics for the generation of optical gain in both material sets, as well as the mechanisms for controlling optical properties of photonic crystals. We then discuss the design, simulation, fabrication, and characterization of organic and quantum dots lasers. We conclude by outlining the future of these projects and the discuss the outlook for organic and quantum dot nanobeam lasers.

1 The reported finesse was 50,000. The Q was calculated by: $Q = \mathcal{F}_\lambda \frac{\lambda}{2\lambda_{\text{r}}}$.  
2 The reported mode volume was $100 \, \mu m^3$. The mode volume was converted to units of $\left(\frac{\lambda}{n}\right)^3$ by setting $\lambda = 920\, \text{nm}$ and $n = 1$ for air.  
3 The mode volume of this device was not reported, and so it was estimated from information about a smaller ring resonator. The mode volume from a smaller ring resonator, which was reported to be $2 \, \mu m^3[18]$, was scaled by the ratio of the areas and radii for the two devices, and then converted to units of $\left(\frac{\lambda}{n}\right)^3$. In fact, the larger resonator, for which the mode volume was estimated, was made of Si$_3$N$_4$ and so will not confine the light as strongly as smaller the Si resonator, signifying that the number calculated for the table is more of a lower bound.
Chapter 2

Light-Matter Interactions

Before we can build lasers, we need to understand the physics of light-matter interactions so that we can generate optical gain. We will quantize the electromagnetic field (using the so-called "second quantization picture") and show that by inserting the vector potential into the Hamiltonian we can derive the absorption and emission rates.\(^1\) This treatment borrows heavily from the book "Introductory Applied Quantum and Statistical Mechanics" by Hagelstein, Senturia, and Orlando, and is suggested as a reference for more information.

2.1 Interaction Picture

A general Hamiltonian for describing the light-matter interaction of a single particle in an electromagnetic field is given by:

\[
\hat{H} = \frac{(\hat{p} - q\hat{A}/c)^2}{2m}
\]  

\(^1\)The way that Einstein derived the absorption and emission rates was by carefully considering a blackbody in equilibrium with its environment, and by making a detailed balance argument. This treatment requires only the Planck spectrum, and careful attention to detail. Though it makes sense that both classical and quantum mechanical descriptions of the same phenomenon must converge, it is nevertheless impressive that they arrive at the same result using such radically different approaches.
which we can expand:

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{q}{2mc} \left( \hat{\rho} \cdot \hat{A} + \hat{A} \cdot \hat{\rho} \right) + \frac{q^2 \hat{A}^2}{2mc^2} \quad (2.2)$$

We recognize the first term as the kinetic energy of the matter, and the last term is the electromagnetic field energy. The middle term describes the interaction of the two particles, and so we will focus our attention on it. We rename this term the interaction Hamiltonian given by:

$$\hat{H}_{int} = -\frac{q}{2mc} \left( \hat{\rho} \cdot \hat{A} + \hat{A} \cdot \hat{\rho} \right) \quad (2.3)$$

The quantized vector potential operator is given by:

$$\hat{A} = \frac{1}{\sqrt{V}} \sum_{k,\alpha} \sqrt{\frac{2\pi \hbar c^2}{\omega_k}} \hat{e}_\alpha(k) \left( \hat{a}_{k,\alpha}^\dagger + \hat{a}_{k,\alpha} \right) e^{ik \cdot r} \quad (2.4)$$

where \( k \) is the photon momentum and \( \hat{e}_\alpha(k) \) is the polarization. We plug into the interaction Hamiltonian:

$$\hat{H}_{int} = -\frac{q}{2mc} \sum_{k,\alpha} \sqrt{\frac{2\pi \hbar c^2}{V \omega_k}} \hat{\rho} \cdot \hat{e}_\alpha(k) \left( \hat{a}_{k,\alpha}^\dagger + \hat{a}_{k,\alpha} \right) e^{ik \cdot r} \quad (2.5)$$

Now we will want to consider how this Hamiltonian will couple states, which we write as:

$$|\psi, n_{k,\alpha}\rangle \quad (2.6)$$

denoting the state of the atom or molecule by \( \psi \) and the number of photons of a certain momentum and polarization by \( n_{k,\alpha} \). We know from first order perturbation theory that the rate of an initial state coupling to a final state in a continuum is given by Fermi’s Golden Rule:

$$S_{if} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{H}_{int} | \psi_i \rangle|^2 \rho(E_f) \quad (2.7)$$
We notice that the transition rate depends on the expectation value of the interaction Hamiltonian, as well as the density of states for the final state. When we sum over all of the final states, we can find the total transition rate, which corresponds to the decay rate of that initial state. We insert our interaction Hamiltonian, and we focus our attention on the matrix element to gain insight about single photon processes. This matrix element is of the form:

\[
\langle \Psi', n_{k',\alpha} | \hat{H}_{int} | \Psi, n_{k,\alpha} \rangle = -\frac{q}{2mc} \sum_{k,\alpha} \sqrt{\frac{2\pi \hbar c^2}{V \omega_k}} \langle \Psi', n_{k',\alpha} | \hat{p} \cdot \hat{c}_\alpha (\hat{a}_{k,\alpha}^\dagger + \hat{a}_{k,\alpha}) e^{ikr} | \Psi, n_{k,\alpha} \rangle
\]  

(2.8)

We now only consider a single photon mode, although the results we will show are applicable to all modes. We are not considering the case of inelastic photon scattering, although the formula we wrote down is general enough to handle that case. Since we are only considering a single mode, we need only consider the cases for which there is a nonzero matrix element, namely, where the initial and final state differ in photon number by only one. For simplicity, we will make the dipole approximation by taking the first term of the taylor expansion of \( e^{ikr} = 1 + ik \cdot r + \ldots \) which is valid in the limit of small \( k \cdot r \) (for an atom this is on the order of the fine structure constant \( \alpha \approx 1/137 \)). In this case we will consider the interaction Hamiltonian matrix element:

\[
\langle \Psi', n_{k,f} | \hat{H}_{int} | \Psi, n_{k,i} \rangle = -\frac{q}{2mc} \sqrt{\frac{2\pi \hbar c^2}{V \omega_k}} \langle \Psi', n_{k,f} | \hat{p} \cdot \hat{c} (\hat{a}_{k}^\dagger + \hat{a}_{k}) | \Psi, n_{k,i} \rangle
\]  

(2.9)

2.1.1 Absorption

Absorption is the process in which an atom or molecule absorbs a photon and is excited to a higher energy state. To consider the case of the absorption of a photon,
first we recall the action of the lowering operator:

\[ \hat{a}|n\rangle = \sqrt{n}|n-1\rangle \]  

(2.10)

If we consider our final state to have 1 fewer photon in the mode than the initial state, then the matrix element is:

\[
\langle \Psi', n_{k,f} | \hat{H}_{\text{int}} | \Psi, n_{k,i} \rangle = -\frac{q}{2mc} \sqrt{\frac{2\pi \hbar c^2}{V \omega_k}} \langle \Psi', n_k - 1 | \hat{p} \cdot \vec{e} (\hat{a}_k) | \Psi, n_k \rangle = \]

\[
-\frac{q}{2mc} \sqrt{\frac{2\pi \hbar c^2}{V \omega_k}} \sqrt{n_k} \langle \Psi' | \hat{p} \cdot \vec{e} | \Psi \rangle \] 

(2.11)

which depends on \( \sqrt{n} \). We now plug the matrix element back into our expression for the absorption rate:

\[
S_{\text{abs}} = \frac{q^2}{4m^2c^2} \frac{2\pi \hbar c^2}{V \omega_k} n_k |\langle \Psi' | \hat{p} \cdot \vec{e} | \Psi \rangle|^2 \rho(E_f) 
\] 

(2.12)

We see that the absorption rate is proportional to \( n \), the number of photons in the mode.

### 2.1.2 Emission

An excited atom or molecule can also relax back down to its ground state, and emit a photon into an available mode. We recall the action of the raising operator:

\[ \hat{a}^\dagger |n\rangle = \sqrt{n+1}|n+1\rangle \] 

(2.13)
If we consider our final state to have 1 more photon in the mode than the initial state, then the matrix element is:

\[
\langle \Psi', n_{k,f} | \hat{H}_{\text{int}} | \Psi, n_{k,i} \rangle = -\frac{q}{2mc} \sqrt{\frac{2\pi\hbar c^2}{V\omega_k}} \langle \Psi', n_{k}+1 | \hat{p} \cdot \hat{e} \left( \hat{a}_{k}^{\dagger} \right) | \Psi, n_{k} \rangle = -\frac{q}{2mc} \sqrt{\frac{2\pi\hbar c^2}{V\omega_k}} \sqrt{n+1} \langle \Psi' | \hat{p} \cdot \hat{e} | \Psi \rangle
\]

which depends on \( \sqrt{n+1} \). Plugging back into our expression for the emission rate:

\[
S_{\text{em}} = \frac{q^2}{4m^2c^2} \frac{2\pi\hbar c^2}{V\omega_k} (n_{k}+1) \langle \Psi' | \hat{p} \cdot \hat{e} | \Psi \rangle^2 \rho(E_f) \tag{2.15}
\]

we see that the emission rate is proportional to \( n + 1 \). A key observation here is that even if the photon number is zero, the emission rate is not zero. Because of spontaneous emission, an atom or molecule that is excited can still emit a photon into a mode containing no other photons. However, we notice that when \( n \) becomes large, the emission rate increases linearly, due to stimulated emission.

To simplify our approach later on, we will break the emission rate into two terms, the spontaneous and stimulated emission rates, such that:

\[
S_{\text{stim}} = \frac{q^2}{4m^2c^2} \frac{2\pi\hbar c^2}{V\omega_k} n_{k} \langle \Psi' | \hat{p} \cdot \hat{e} | \Psi \rangle^2 \rho(E_f) \tag{2.16}
\]

\[
S_{\text{spom}} = \frac{q^2}{4m^2c^2} \frac{2\pi\hbar c^2}{V\omega_k} \langle \Psi' | \hat{p} \cdot \hat{e} | \Psi \rangle^2 \rho(E_f)
\]

\[\]

2.2 Laser Theory

Now that we have calculated the absorption and emission rates, we can put them together to understand the dynamics that govern lasing. Our treatment borrows from the approach used in the book "Diode Lasers and Photonic Integrated Circuits" by Coldren, Corzine, and Mashanovitch, and is recommended as a reference. If we consider the states that couple via the interaction Hamiltonian under the absorption
or emission of light of a single mode, we make the implicit assumption that we are working with a 2 level system. If we now make the assumption that both states have the same level of degeneracy, such as atomic or molecular orbitals with each a spin up and spin down state, we notice that the stimulated emission and absorption rates are identical, and that both processes are equal to the spontaneous emission rate multiplied by the number of photons in the mode. Though these assumptions can later be relaxed, we will use them for now to simplify our problem so that we can understand the physics of lasing. We can write down a rate equation for the number of excited states in our two level system assuming that it couples to the ground state by only a single mode:

\[
\frac{dn}{dt} = k_{abs} P_g (1 - P_e) - k_{stim} P_e (1 - P_g) - k_{spon} P_e (1 - P_g) = +k_{spon} P_g (1 - P_e) n_p - k_{spon} P_e (1 - P_g) n_p - k_{spon} P_e (1 - P_g) = -k (P_e - P_g) n_p - k P_e (1 - P_g)
\]

(2.17)

\(P_e\) and \(P_g\) are the probabilities of being in the excited and ground states respectively, and \(k\) is the rate that is equal for all terms, though we originally defined it as the spontaneous emission rate.

We now begin to think about how the single mode rate equation relates to energy flow in an absorbing or gain producing material. We know from Beer's law that the optical power is attenuated exponentially in an absorbing material. If we consider a gain material, a similar relation is true:

\[P(z) = P_0 e^{g z}\]

(2.18)

where \(g\) is the gain coefficient, with units of inverse length. We know that the optical power is proportional to the number of photons, and we rewrite our Beer's law-like equation in differential form:

\[\frac{dn_p}{dz} = g(N) n_p\]

(2.19)

We make explicit the dependence of the gain coefficient on the density of excited
states $N$, not to be confused with the number of excited states $n$. We can convert the $z$ dependence to a time dependence by knowing that the energy velocity is given by the group velocity of the mode:

$$\frac{dn_p}{dt} = v_g g(N)n_p$$

(2.20)

If our gain material is producing extra photons, we assume that each comes from the deactivation of an excited state, so we can relate the number of photons to the number of excited states:

$$\frac{dn}{dt} = -v_g g(N)n_p$$

(2.21)

Looking at equation 2.17 and comparing with the expression we just derived, we see that a logical way to define the gain coefficient is the net stimulated emission rate minus the absorption rate. We rewrite our single mode rate equation:

$$\frac{dn}{dt} = -v_g g(N)n_p - v_g g(N)\frac{P_c(1-P_g)}{P_c - P_g}$$

(2.22)

The expression $\frac{P_c(1-P_g)}{P_c - P_g}$ is important in a semiconductor laser, where there are many states in both the valence and conduction bands, and the fraction of states in either band varies continuously. However, in organic semiconductors and quantum dots, the number of states on any emitter are very few. This leads to a binary distribution of the states, either being excited or not, so we can work in the limit of the asymptotic behavior of the expression. In the limit that $P_c \to 1$, $\frac{P_c(1-P_g)}{P_c - P_g} \to 1$, so we can neglect this expression.

$$\frac{dn}{dt} = -v_g g(N)n_p - v_g g(N)$$

(2.23)

Our rate equation is coming along nicely, but we need to begin to account for some of the assumptions we made earlier, and reconcile the ones that will not be general enough to describe our photonic crystal lasers. One assumption we made is that the photon is traveling in a pure gain material. For our lasers, the photons are
not perfectly confined to gain material. They travel through other waveguide material as well as air. As is done in the literature, we introduce the "confinement factor" \( \Gamma \equiv \frac{V_{\text{act}}}{V_{\text{ph}}} \), where \( V_{\text{act}} \) is the region of optically active absorbing or emitting material, and \( V_{\text{eff}} \) is the mode volume, defined in the literature as \( V_{\text{eff}} = \frac{\int \kappa(r)|E(r)|^2 d^3r}{\max_{\kappa(r)}|E(r)|^2} \). [19]. Any place that the gain coefficient comes into the rate equations we can multiply by the confinement factor to account for the fact that absorption and emission processes only happen in the volume of the optically active materials, rather than the entire volume that the mode sees. We rewrite our rate equation:

\[
\frac{dn}{dt} = -v_g \Gamma g(N)n_p - v_g \Gamma g(N) \tag{2.24}
\]

We also need to account for the fact that other modes exist for which the probability of emission is nonzero. Though we can add them individually into our rate equation, in practice, it becomes difficult to track them all down. To account for these modes, we introduce a factor, \( \beta \) which in the literature is commonly known as the spontaneous emission factor. This factor represents the fraction of total spontaneous emission into the lasing mode. We rewrite our equation:

\[
\frac{dn}{dt} = -v_g \Gamma g(N)n_p - \sum_m v_{gm} \Gamma_m g_m(N) \tag{2.25}
\]

\[
= -v_g \Gamma g(N)n_p - B(N) - \beta B(N) - (1 - \beta) B(N)
\]

but we recall that \( \beta B(N) = v_g \Gamma g(N) \), so we set \( B(N) = \frac{v_g \Gamma g(N)}{\beta} \) and plug back in:

\[
\frac{dn}{dt} = -v_g \Gamma g(N)n_p - v_g \Gamma g(N) - \frac{1 - \beta}{\beta} v_g \Gamma g(N) \tag{2.26}
\]

The corresponding photon number rate equation is:

\[
\frac{dn_p}{dt} = +v_g \Gamma g(N)n_p + v_g \Gamma g(N) - \frac{n_p}{\tau_{\text{cavity}}} \tag{2.27}
\]
We introduced the idea of the cavity back when we added in the confinement factor. But we now consider the effect of the cavity on the local density of optical modes, a concept which we will discuss in more detail in the next chapter. Our photonic crystal cavity will increase the density of modes for the cavity mode, and suppress the other modes. This effect is pronounced for cavities with high \( Q/V \) ratios, and is called the Purcell effect. Since the Purcell effect increases the density of modes for the lasing mode, we introduce a Purcell enhancement factor \( F_m \). We also introduce another Purcell factor to signify the suppression of spontaneous emission into the other modes \( F_s \). Since \( \beta \) and \( F_s \) are both related to spontaneous emission into other modes that are difficult to keep track of experimentally, we will combine the two factors to simplify our model so that we can fit with fewer parameters. We define \( F_s \equiv F_m \frac{1 - \beta}{\beta} \).

Before inserting the Purcell factors we need to carefully consider the terms that they modify. In the literature, there has been some discussion as to what processes are enhanced by the Purcell effect. The local density of optical states is enhanced at the cavity resonance, and since the quantum mechanical picture of the spontaneous and stimulated emission rates are the same up to the factor of \( n_p \), they both can see a Purcell enhancement. However, many authors have not included Purcell enhancement in their rate equations for the stimulated emission term [20][21]. A recent paper by Gregerson, Lorke, and Mork examined the Purcell enhancement closely and determined that the stimulated emission rate is only enhanced by the Purcell effect if the linewidth of the cavity is larger than the linewidth of the emitters[22], a result that agrees with past literature[19]. As the cavity Q’s we work with for photonic crystals are high, we will work in a regime that the cavity linewidth is narrower than the emission spectrum, and we will not include a Purcell enhancement for the stimulated emission terms.

Our rate equations now take the form:

\[
\begin{align*}
\frac{dn}{dt} &= -v_g \Gamma g(N)n_p - F_m v_g \Gamma g(N) - F_s v_g \Gamma g(N) \\
\frac{dn_p}{dt} &= v_g \Gamma g(N)n_p + F_m v_g \Gamma g(N) - \frac{n_p}{\tau_{cavity}}
\end{align*}
\]  

(2.28)
It is often the case that working with densities is easier than working with exact numbers. Therefore we transform the equations by dividing the excited state density rate equation by the active volume $V_{act}$ and the photon number rate equation by the mode volume $V_{eff}$. Our density rate equations take the form:

\[
\frac{dN}{dt} = -v_g g(N) N_p - \frac{F_m v_g g(N)}{V_{eff}} - \frac{F_s v_g g(N)}{V_{eff}}
\]

\[
\frac{dN_p}{dt} = v_g \Gamma g(N) N_p + \frac{F_m v_g \Gamma g(N)}{V_{eff}} - \frac{N_p}{\tau_{cavity}}
\]

Here we note that different communities use different approximations for the gain. The organics community uses the approximation that the $g(N) = N \sigma_{SE}$ where $\sigma_{SE}$ is the stimulated emission cross section. The semiconductor community uses an approximation that works for a larger range of $N$: $g(N) = g_0 \ln \left( \frac{N}{N_0} \right)$ where $N_0$ is called the transparency density, where the gain coefficient is zero due to the absorption and stimulated emission rates exactly cancel.

If we choose the approximation made in the organics community, our rate equations take the form:

\[
\frac{dN}{dt} = -v_g \sigma_{SE} N N_p - \frac{F_m v_g \sigma_{SE} N}{V_{eff}} - \frac{F_s v_g \sigma_{SE} N}{V_{eff}}
\]

\[
\frac{dN_p}{dt} = v_g \Gamma \sigma_{SE} N N_p + \frac{F_m v_g \Gamma \sigma_{SE} N}{V_{eff}} - \frac{N_p}{\tau_{cavity}}
\]

Now that our rate equations take into account all of the photophysics associate with absorption and emission, we can include extra terms to complete our rate equations, such as nonradiative recombination of excited states, and the pumping of the excited state by some mechanism:

\[
\frac{dN}{dt} = \frac{N}{\tau_{pump}} - v_g \sigma_{SE} N N_p - \frac{F_m v_g \sigma_{SE} N}{V_{eff}} - \frac{F_s v_g \sigma_{SE} N}{V_{eff}} - \frac{N}{\tau_{nr}}
\]

\[
\frac{dN_p}{dt} = v_g \Gamma \sigma_{SE} N N_p + \frac{F_m v_g \Gamma \sigma_{SE} N}{V_{eff}} - \frac{N_p}{\tau_{cavity}}
\]
2.3 Organic Molecules

We turn our attention to organic molecules and how they can be used to generate optical gain. Organic molecules are bound collections of mostly carbon, hydrogen, oxygen, and nitrogen atoms. In the solid state, these molecules are held together by Van der Waals forces. Though molecular solids are held together by attractive forces, most organic molecules share little wavefunction overlap with their neighbors, leading to highly localized wavefunctions. Upon excitation (e.g. by photoexcitation), an electron in the lowest occupied molecular orbital (HOMO) may transition to the lowest unoccupied molecular orbital (LUMO). The excited electron and hole are coulombically attracted to one another, and form a bound state called an exciton. Excitons can be modeled using hydrogenic wavefunctions, with a screened electric field, and thus a larger Bohr radius. Excitons are formed in all semiconducting materials upon photoexcitation, however, their binding energy is often on the order of tens of melectronvolts, which is the same energy scale as thermal energy fluctuations ($k_B T$) and so they dissociate on a time scale of several hundred femtoseconds. These excitons are called Wannier-Mott excitons. In organic semiconductors, the high degree of localization decreases the screening of the electric field that separates the electron-hole pair, giving the exciton a large binding energy on the order of an electron volt. These excitons are called Frenkel excitons.

2.3.1 4 Level Systems

Another important implication of the high degree of localization of molecular wavefunctions is the stokes shift, or Franck-Condon shift, between their absorption and emission spectra. When an electron is excited to the LUMO, the shift in electron density causes the nuclei to no longer be in their equilibrium positions. The molecule then relaxes via a vibrational transition down to the ground vibrational state of the electronic excited state, on a timescale of hundreds of femtoseconds. The electron then relaxes radiatively back to the HOMO, and the nuclei, still configured for the excited electronic state, must then relax back to their original configuration. A schematic
showing these 4 transitions is shown in figure 2-1. This built in 4 level system is what makes organics such good gain materials for lasers: their spectral separation between absorbed and emitted light results in low parasitic self-absorption. Their many vibrational energy levels give them a broad gain spectrum that makes them suitable for tunable lasers.

![Energy Level Diagram](image)

Figure 2-1: Excitation of an organic molecule can be thought of as a 4 level system. The electron is excited to the LUMO and the molecule undergoes vibrational relaxation. The electron then relaxes back down to the HOMO, and upon vibrational relaxation the molecule returns to its original ground state.

### 2.3.2 Singlet and Triplet excitons

In organic molecules, the HOMO holds two electrons of opposite spins, and so by Pauli exclusion principle, the spatial wavefunction has to be symmetric. This configuration of the HOMO wavefunction is a singlet state, and can be described using the representation:

$$|\Psi_{sym}\rangle \otimes \frac{1}{\sqrt{2}}(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle)\) \quad (2.32)$$

Upon absorption of a photon, the electron transitions to the LUMO, and due to selection rules, this excited state must also be singlet. Because the electron in the LUMO and the electron in the HOMO no longer occupy the same state, they can
also have the same spin, with antisymmetric spatial wavefunctions. These states are called triplet states, and are represented by the wavefunctions:

\[
|\Psi_{\text{Antisym}}\rangle \otimes \frac{1}{\sqrt{2}} (|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle) \\
|\Psi_{\text{Antisym}}\rangle \otimes |\uparrow, \uparrow\rangle \\
|\Psi_{\text{Antisym}}\rangle \otimes |\downarrow, \downarrow\rangle
\] (2.33)

Triplet states often have lower energy than singlets do, because their antisymmetric spatial wavefunctions result in less electronic overlap, and less coulomb repulsion between the two electrons. Triplets are not photogenerated due to selection rules, however, they are readily generated by singlet excitons undergoing intersystem crossing, or by current injection. Because the triplet state is forbidden to undergo radiative relaxation back to the HOMO, they have much longer lifetimes than singlet states. While, Singlet lifetimes in organic molecules are on the order of nanoseconds, triplet lifetimes can be microseconds, milliseconds, or longer, and these long lifetimes are problematic for trying to achieve electrical pumping and continuous wave operation of organic lasers[23].

2.3.3 Exciton Transport

Excitons can be transported from molecule to molecule in a solid by either Dexter energy transfer or by Förster resonance energy transfer (FRET). Dexter energy transfer is basically the simultaneous tunneling of an electron in the HOMO and an electron in the LUMO of a neighbor molecule switching places. Since the energy transfer process is via tunneling, the rate of Dexter energy transfer is exponentially dependent on the distance separating the molecules. In contrast with Dexter transfer, FRET is a process by which one molecule emits a virtual photon that is absorbed by a neighboring molecule. In order for FRET to occur, the emission spectrum of the donor and absorption spectrum of the acceptor must overlap spectrally. FRET is a dipole-dipole interaction, so it has a dependence of \(1/R^6\). Because FRET is less sensitive to distance, it has a much higher rate than Dexter transfer, often on the
order of picoseconds, and it results in an exciton diffusion length that is between 10 and 100 nm. Figure 2-2 shows schematics comparing the exciton transport pathways.

![Schematics for Dexter and Förster energy transfer](image)

Figure 2-2: Here we show schematics for (a) Dexter energy transfer and (b) Förster resonance energy transfer.

### 2.4 Optical Gain in Quantum Dots

Quantum dots (QDs) are semiconductor nanocrystals formed either by epitaxial growth or in solution, which are known as colloidal quantum dots. Colloidal QD’s tend to be more monodisperse, and can be encapsulated with organic ligands to form stable, highly emissive nanoparticles that are solution processable. Though QDs are made of covalently bonded semiconductors, their energy landscape is similar to organic molecules, due to their small size and highly localized wavefunctions. This localization of charge gives rise to three dimensional particle-in-a-box like states in both the conduction and valence bands, and the bandgap is determined by the energy spacing between these states. As with a three dimensional particle-in-a-box, the density of states looks like a series of delta functions. These discrete states give QDs a sharp peak in their absorption and emission spectra, which is limited by inhomogeneous broadening. By changing the radius of the quantum dot, the confinement
and therefore energy levels of the electronic states are shifted, and this allows for the tuning of the absorption and emission spectra.

Early colloidal quantum dots were made of a single semiconductor alloy. However, the introduction of a shell material grown around the core using different semiconductor alloys enables the creation of a heterojunction. By forming type I and type II heterojunctions, the localization of charge and the energy levels of the conduction and valence bands can be tuned. Figure 2-3 shows both types of QD heterostructures.

![Diagram of Type I and Type II heterojunctions]

**Figure 2-3:** A common structure for colloidal quantum dots is a core of one semiconductor alloy with a shell of another alloy grown around it. The structure is encapsulated with organic ligands to passivate the surface states and increase radiative efficiency. Shown above are QDs where the core and shell semiconductor bands form type I and type II heterojunctions.

Though quantum dots share the same localization of charge as molecules that leads to sharp excitonic features, they do not necessarily have a built in 4 level system. Because of the covalently bonded lattice, the vibrational energy levels are spaced much closer together than in organics, leading to smaller stokes shifts. Therefore, a
2 level system is a more appropriate way to model the valence and conduction band states for QDs, compared to a 4-level system.

The first demonstrations of optical gain generated in QDs involved simply exciting multiple excitons, resulting in a highly inverted system, but requiring a large threshold excitation density of around 2 mJ/cm², which is about 3 orders of magnitude higher than for organics[24]. It was clear that the threshold for optical gain could be dramatically reduced by single exciton gain. However, in a 2 level system in which the ground and excited states are degenerate, single exciton gain is not possible, due to cancellation between the stimulated emission and absorption rates. The community demonstrated successfully single exciton gain in 2007 by breaking the degeneracy of the conduction band by use of a type II heterojunction QD[25]. A core-shell quantum dot was used where the shell had a lower conduction energy level than the core, spatially separating the charges of the excited exciton. This spatial separation created an internal electric field, which introduced a stark shift in the excited state energy level for the other exciton. A schematic outlining this technique is shown in figure 2-4. Though the degeneracy in the conduction band was lifted, it came at the expense of

![Figure 2-4: Single exciton gain is achieved by a type II heterojunction core-shell quantum dot. The exciton is split between the shell and core. This spatial separation of charge results in an internal electric field, which stark shifts the excited state of the other exciton. By breaking the degeneracy of the excited states, there is no longer a 2 level system, and single exciton gain is made possible.](image-url)
spatial separation of the electron-hole pair, which decreased the oscillator strength, and did not result in a dramatic reduction in gain threshold.

Finally, in 2012, the community demonstrated successful single exciton gain in a type I heterojunction core-shell quantum dot[3]. By growing a ternary alloy of Cd$_{0.5}$Zn$_{0.5}$S around a core of CdSe, the Nurmikko group broke the degeneracy of the valence band. Their quantum dots were not perfectly spherical, but had a pyramidal shape which they explained helped them break the spin degeneracy of the valence band. Figure 2-5 shows a TEM image from their paper of these quantum dots. They demonstrated lasing at thresholds of 90 μJ/cm$^2$ using a microcavity structure formed by sandwiching a layer of quantum dots between two mirrors, a threshold which is comparable to early organic lasers.

![TEM image of quantum dots](image)

Figure 2-5: TEM image of quantum dots used by the Nurmikko group to achieve single exciton gain. [3]
Chapter 3

Photonic Crystals

Photonic crystals are given their name because of the analogy made between them and solid crystalline materials. We know from solid state physics that by placing atoms in a periodic lattice, we expect the energy levels of electrons to form bands which may contain bandgaps depending on the shape and strength of the potential. We will rely on our intuition from quantum mechanics to develop our understanding of how a photonic crystal creates bands and band gaps for photonic states. Photonic crystals represent an entire research field just by themselves, and so the formalism required to develop a complete picture of their physics is beyond the scope of this thesis. For curious readers who want to understand photonic crystals on a deeper level, I highly recommend the free online book “Photonic Crystals: Molding the Flow of Light” by Joannopoulos, Johnson, Winn, and Meade as a starting point, which can be found here: \texttt{http://ab-initio.mit.edu/book/photonic-crystals-book.pdf}. In fact, the abbreviated treatment of photonic crystals in this thesis borrows heavily from this book.
3.1 Maxwell’s Equations as an Eigenvalue Problem

To understand classical light propagation in a photonic crystal we can begin with Maxwell’s equations.

\[
\begin{align*}
\nabla \cdot \mathbf{B} &= 0 \\
\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} &= 0 \\
\nabla \cdot \mathbf{D} &= \rho \\
\nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} &= \mathbf{J}
\end{align*}
\]  \quad (3.1)

We make several approximations: that we work in linear, transparent media, with no free charges, and we will work with only real, positive permittivities \( \varepsilon(r) \). This means that \( \mathbf{D} = \varepsilon_0 \varepsilon(r) \mathbf{E}(r) \), and \( \mathbf{H} = \mu_0 \mu_r(r) \mathbf{B}(r) \), however for most materials near optical frequencies, \( \mu_r(r) \approx 1 \). We rewrite Maxwell’s equations:

\[
\begin{align*}
\nabla \cdot \mathbf{H}(r,t) &= 0 \\
\nabla \times \mathbf{E}(r,t) + \frac{\partial \mathbf{H}(r,t)}{\partial t} &= 0 \\
\nabla \cdot [\varepsilon(r) \mathbf{E}(r,t)] &= 0 \\
\nabla \times \mathbf{H}(r,t) - \frac{\partial \mathbf{E}(r,t)}{\partial t} &= 0
\end{align*}
\]  \quad (3.2)

Since Maxwell’s equations are now linear, we can assume that the solutions are time harmonic:

\[
\begin{align*}
\mathbf{E}(r,t) &= \mathbf{E}(r)e^{-i\omega t} \\
\mathbf{H}(r,t) &= \mathbf{H}(r)e^{-i\omega t}
\end{align*}
\]  \quad (3.3)

Thinking about the types of solutions that will satisfy Maxwell’s equations, we consider plane wave solutions, such as \( \mathbf{H}(r) = H_0 \exp(ik \cdot r) \). We can automatically satisfy the divergence being zero by enforcing the condition that \( \mathbf{H}_0 \cdot \mathbf{k} = 0 \). We turn our attention to the other two equations and plug in our solutions:

\[
\begin{align*}
\nabla \times \mathbf{E}(r) - i\omega \mu_0 \mathbf{H}(r) &= 0 \\
\nabla \times \mathbf{H}(r) + i\omega \varepsilon_0 \varepsilon(r) \mathbf{E}(r) &= 0
\end{align*}
\]  \quad (3.4)
and with some algebraic manipulation of equations 3.4 we arrive at:

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

(3.5)

Which becomes an eigenvalue problem, with the linear operator \( \mathbf{\Theta} = \nabla \times \frac{1}{\epsilon(r)} \nabla \times \) operating on the magnetic field yielding eigenvalues \( \left( \frac{\omega}{c} \right)^2 \). We will not prove it here, but it can be shown that given our assumptions about \( \epsilon(r) \), \( \mathbf{\Theta} \) is a Hermitian operator.

We can now find the electric field by plugging into the equation:

$$\mathbf{E}(r) = \frac{i}{\omega \epsilon_0 \epsilon(r)} \nabla \times \mathbf{H}(r)$$

(3.6)

Since the curl of a divergence is always zero, finding the electric field by plugging into equation 3.6 will always guarantee that Gauss’s law is enforced.

Recasting Maxwell’s equations in the form of an eigenproblem allows us to make comparisons between quantum mechanics and electrodynamics and draw parallels between them to help build our intuition. See table 3.1 for the comparison.

Table 3.1: Comparison between quantum mechanics and electrodynamics

<table>
<thead>
<tr>
<th>Field</th>
<th>Quantum Mechanics</th>
<th>Electrodynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field</td>
<td>( \Psi(r, t) = \Psi(r)e^{iEt/\hbar} )</td>
<td>( \mathbf{H}(r, t) = \mathbf{H}(r)e^{-i\omega t} )</td>
</tr>
<tr>
<td>Eigenvalue Problem</td>
<td>( \hat{H}\Psi = E\Psi )</td>
<td>( \mathbf{\Theta}\mathbf{H} = \left( \frac{\omega}{c} \right)^2 \mathbf{H} )</td>
</tr>
<tr>
<td>Hermitian Operator</td>
<td>( \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) )</td>
<td>( \mathbf{\Theta} = \nabla \times \frac{1}{\epsilon(r)} \nabla \times )</td>
</tr>
</tbody>
</table>

### 3.2 Symmetry

Now that we have an equation to solve, we might wonder what the solutions to Maxwell’s equations look like. Of course, the solutions depend on the geometry of the problem. We start by considering systems that have continuous translational symmetry. For these systems, we can translate them by a distance \( d \) and recover a solution of the same functional form. The equivalent mathematical statement involves
operating on a state with the translation operator $\hat{T}_d$. If we recover a solution that is of the same functional form, then that state is an eigenfunction. A system that has translational symmetry along the $z$ direction is invariant under any translations along the $z$ direction, up to a phase. We translate a distance $d$ along the $z$ direction:

$$\hat{T}_d e^{ikz} = e^{ik(z-d)} = e^{-ikd} e^{ikz}$$  \hspace{1cm} (3.7)

Though we need group theory to prove it, we cite the result that the eigenfunctions of the translation operator are of the functional form $e^{ikr}$ if the system has translational symmetry in all three directions. Since the translation operator commutes with the Maxwell operator we defined earlier $\hat{\Theta}$ that means the eigenfunctions of $\hat{\Theta}$ share the same functional form as the eigenfunctions of $\hat{T}$, namely:

$$H_k(r) = H_0 e^{ikr}$$  \hspace{1cm} (3.8)

which are plane waves that we categorize by a particular $k$. If we had instead a system with only translational symmetry in the $z$ direction, the eigenfunction would take a form:

$$H_k(r) = H_0(x,y) e^{ikz}$$  \hspace{1cm} (3.9)

It is important to note that any place symmetry is broken along a particular direction, the functional form of the eigenfunction changes as well, and the corrollary to this statement is that any time we have translational symmetry in a direction, than the component of $k$ in that direction is conserved. We will take advantage of this idea for much more complicated structures, involving different symmetries, but the principle will remain the same.

### 3.3 Periodicity and Bloch Modes

We now consider a system with discrete translational symmetry, such that the system is symmetric with respect to translations of discrete movements $a$. Here $a$ is called
the lattice constant, as it describes the periodicity of the lattice. We know that the translation operator \( \hat{T}_d \) commuted with \( \hat{\Theta} \) for all distances \( d \) if the system had continuous translational symmetry, but for the case of discrete translational symmetry, only \( \hat{T}_{na\hat{c}} \) will commute with \( \hat{\Theta} \), where \( n \) is an integer and \( \hat{a} \) is the direction along the periodicity. We call the set of \( na\hat{c} \) the lattice vectors \( \mathbf{R} \). Since \( \hat{T}_\mathbf{R} \) commutes with \( \hat{\Theta} \), the eigenfunctions of \( \hat{T}_\mathbf{R} \) must also be eigenfunctions of \( \hat{\Theta} \).

\[
\hat{T}_\mathbf{R} e^{i\mathbf{k} \cdot \mathbf{r}} = e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R})} = e^{-i\mathbf{k} \cdot \mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{r}}
\]

We can continue classifying modes using the labels \( k \) for our solutions. One key difference here is that due to the periodicity of the system, we can choose values of \( k \) that differ by \( m \frac{2\pi}{a} \), where \( m \) is an integer, and get back the same eigenvalue. We call \( \frac{2\pi}{a} \) the reciprocal lattice constant, and define the set of reciprocal lattice vectors \( \mathbf{K} \) the integer multiples of the reciprocal lattice constant, because in the same way that we can translate \( \mathbf{r} \) in real space by any \( \mathbf{R} \) and get back the same solution, we can translate our \( k \) by a reciprocal lattice vector \( \mathbf{K} \) and get back the same solution, up to a phase. Since linear combinations of degenerate eigenfunctions yield the same eigenvalues, we can construct solutions to \( \hat{\Theta} \) with linear combinations of eigenfunctions of the discrete translation operator;

\[
\mathbf{H}_k(\mathbf{r}) = \sum_{\mathbf{K}} c_{k,\mathbf{K}}(\mathbf{r}) e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}}
= e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{K}} c_{k,\mathbf{K}}(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}}
= e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{u}_k(\mathbf{r})
\]

The result that we can rewrite any solution as just a plane wave times a periodic function is called Bloch’s theorem. We notice that by labeling these states by the wavevector \( k \) we only need to consider states whose \( k \)s are inside the first Brillouin zone. An example of this is in a 1D lattice for the x direction, is that we would only need to consider \( k_x \in \left( \frac{-\pi}{a}, \frac{\pi}{a} \right] \).
3.4 Photonic Crystals, Band Structures

For a photonic crystal, we can now plug in the solutions from above into our eigenvalue problem:

\[
\hat{\Theta}H_k = \left( \frac{\omega(k)}{c} \right)^2 H_k
\]

\[
\nabla \times \frac{1}{\epsilon(r)} \nabla \times e^{ikr}u_k(r) = \left( \frac{\omega(k)}{c} \right)^2 e^{ikr}u_k(r)
\]

\[
(\nabla + ik) \times \frac{1}{\epsilon(r)} (\nabla + ik) \times u_k(r) = \left( \frac{\omega(k)}{c} \right)^2 u_k(r)
\]

\[
\hat{\Theta}_k u_k(r) = \left( \frac{\omega(k)}{c} \right)^2 u_k(r)
\]

We have now defined a new Hermitian operator \( \hat{\Theta}_k \) that operates on our mode profiles \( u_k(r) \). The mode profiles \( u_k(r) \) are periodic such that \( u_k(r) = u_k(r + R) \) and must obey the condition \( \nabla + ik u_k(r) = 0 \). Within this context, \( k \) varies continuously inside the Brillouin zone, giving us smooth bands of \( \omega \) in reciprocal space.

As an example, we will now solve for the bandstructure of a two dimensional photonic crystal shown in figure 3-1. Our structure is a square lattice of air holes in dielectric with a refractive index of 1.7 (close to that of many organic materials and bulk films of quantum dots). When plotting the bandstructure in figure 3-2, we plot a region called the light cone, denoting all of the modes that are allowed to propagate in free space. Any modes that lie under the light cone are localized to the photonic crystal, and may propagate inside, but these modes will evanescently decay into free space. The border between the light cone and the localized modes is called the "light line" and is given by \( \omega = c|k| \). We separate the solutions into the modes that have transverse electric (TE) and transverse magnetic (TM) fields, where TE denotes an electric field in the plane of the photonic crystal, and TM denotes a magnetic field in the plane of the photonic crystal.

We see that for a two dimensional photonic crystal where the high index material is organic, a photonic band gap in either the transverse electric (TE) or transverse magnetic (TM) modes is difficult to achieve. If we simply consider moving to a
Figure 3-1: Here we consider photonic crystal, depicted in (a) formed by a 2 dimensional square lattice with lattice constant $a = 280$ nm. The lattice is formed by periodic placement of air holes of $n = 1$ with radius $r = 117$ nm into a higher index material with $n = 1.7$. (b) shows the representation of the lattice in reciprocal space, with points of high symmetry marked by the letters $\Gamma$, $X$, and $M$.

Figure 3-2: The bandstructure of the photonic crystal is shown along the directions connecting the high symmetry points in reciprocal space.

one dimensional photonic crystal, we can eliminate the $M$ high symmetry point in reciprocal space, and our irreducible Brillouin zone is restricted to a straight line between the $\Gamma$ and $X$ points. The bandstructure is effectively truncated at the $X$
point of our plot, resulting in the new plot shown in figure 3-3. We see that there are now photonic bandgaps for both the TE and TM guided modes, around 400 THz.

![Figure 3-3: Truncating the bandstructure to 1D, we see that there are photonic band gaps in both the TE and TM modes.](image)

We have created a photonic bandgap, and we will now examine the factors that affect the gap size and band edge frequencies. We will zoom in on the band edges near $k \cdot (\frac{2\pi}{a}) = 0.5$ so that we can get a better idea of how the bands shift by changing parameters of the photonic crystal. By using perturbation theory, though we will not show the derivation here, it can be shown[26] that the size of a bandgap for a one dimensional photonic crystal is given by the expression:

$$\frac{\Delta \omega}{\omega_{midgap}} = \frac{\Delta \epsilon}{\epsilon} \frac{\sin(\pi d/a)}{\pi}$$  \hspace{1cm} (3.13)

For organic, due to their low refractive index, we will be at somewhat of a disadvantage compared to creating photonic crystals in high index materials like silicon. However, we can still adjust the bandgap by changing the geometric parameters of the photonic crystal. By decreasing the hole radii, we effectively increase the amount of dielectric that the modes will see. The increase in the amount of dielectric pulls
the bands away from the light line. However, with the small index contrast between dielectric and air, it will also noticeably decrease the size of the gap. Figure 3-4 shows both the TE and TM one dimensional bandstructure of a photonic crystal with fixed lattice constant $a = 280$ nm and varying hole radii $r = \{120 \text{ nm}, 100 \text{ nm}, 80 \text{ nm}\}$.

![Figure 3-4: The TE (a) and TM (b) bandstructures are plotted for a fixed lattice constant of $a = 280$ nm and with varying hole radii $r = \{120 \text{ nm}, 100 \text{ nm}, 80 \text{ nm}\}$.](image)

Similarly we can adjust the bandstructure by changing the lattice constant $a$. If the holes are kept the same radius, a decrease of $a$ reduces the amount of dielectric material separating the holes. We saw that increasing the dielectric pushed the bands away from the light line. In our case we are decreasing the amount of dielectric, which will push the bands up towards the light line. Figure shows both the TE and TM 1D bandstructure of a photonic crystal with a fixed hole radius $r = 100$ nm and with varying lattice constant $a = \{280 \text{ nm}, 260 \text{ nm}, 240 \text{ nm}\}$.

### 3.5 Defects and Cavities

Now that we understand how to create photonic bandstructures, we can begin to think about how to utilize them to create a microcavity. We showed in equation 3.11 that the Bloch modes are periodic with respect to each unit cell. This means that for a given mode, the solution for each unit cell is identical up to a phase factor. If we now consider perturbing the photonic crystal by changing one of the unit cells, we will not affect the solution for the rest of the unit cells, but the local solution for
Figure 3-5: The TE (a) and TM (b) bandstructures are plotted for a fixed hole radius $r = 100 \text{ nm}$ and with varying lattice constant $a = \{280 \text{ nm}, 260 \text{ nm}, 240 \text{ nm}\}$.

the unit cell that has been perturbed will be different. A propagating solution that encounters this defect will do either of two things: it may scatter either to a different $k$-state with the same frequency, if it exists, or it will “tunnel” through the defect, with some fraction of the mode reflected due to the impedance mismatch between the defect and the rest of the photonic crystal.

By removing a hole or changing the hole radius for a unit cell, the bands of the local solutions of that single unit cell will shift, but the rest of the crystal will see a negligible change, especially if the number of unit cells is large. We can engineer a cavity mode by placing a defect in the crystal such that a defect mode exists inside the photonic bandgap for the rest of the crystal. Furthermore, if instead of producing a point defect, we slowly vary a parameter over a large distance, then we can shift the bands in an adiabatic fashion, which will minimize scattering. Figure shows an example of a cavity mode for a one dimensional photonic crystal:

As we will see later, the manner in which a geometric property is varied will determine the strength of confinement of the cavity mode. Finally, we can define a dimensionless parameter called the quality factor which is a measure of how long a electromagnetic energy is stored in a cavity mode:

$$Q = 2\pi \times \frac{\text{EnergyStored}}{\text{EnergyLostpercycle}} = \frac{\nu}{\Delta \nu}$$

(3.14)
Chapter 4

Organic Nanobeam Lasers

Now that we understand the physics of each constituent component of a laser, we can begin to think about assembling them. A well studied host-guest system used for lasing is tris(8-hydroxyquinolinato)aluminium (Alq3) and 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM)[8][9]. We will use the optimal DCM doping fraction of 2.5%, which balances a higher number of emitters against an increase in self absorption as the DCM fraction is increased[27]. The chemical structures of Alq3 and DCM are shown in Figure 4-1. The fraction of DCM in a composite film is small, so for the purposes of cavity design we approximate the index of refraction of the film as just the index of refraction of Alq3: n ≈ 1.7 around 600 nm[28].
4.1 Practical Considerations

When designing the cavity, there is a lot of flexibility in the design, but one must take into account practical considerations such as feasibility of fabrication. We begin by considering the method of deposition of the organic material. Alq3 and DCM are usually thermally evaporated, so we will blanket the surface of whatever structure we have with organic molecules. We want to create a nanobeam photonic crystal cavity, so the structure will have to be free standing. Since the index of refraction of the organic layer is around 1.7, we need to create a waveguide support structure that is of a lower index material. We also create features that are on the order of the wavelength of light, so we need to use electron beam lithography to create the pattern. Like most resists, ebeam resists come in positive and negative tone varieties. Positive resists are exposed and removed in the development step. The opposite occurs in negative resists, meaning that the unpatterned regions are removed by developer. Since we deposit the organic material after doing all of the nanopatterning, it does not matter whether the resist is negative or positive tone. We choose to use a negative tone resist, hydrogen silsesquioxane (HSQ), which is manufactured under the name Dow Corning XR-1541 E-Beam Resist. HSQ is a high sensitivity resist that allows it to have high resolution, which we need to ensure accurate reproduction of our pattern.

4.2 Design

The design of the cavity is based on the nanobeam photonic crystal designs outlined in the literature[29], but for the sake of being self contained we will discuss the design considerations here as well. Figure 4-2 shows a schematic of the structure.

Before getting into the design, we need to specify a target frequency for our lasing mode. We choose 478 THz, near the peak of the DCM gain spectrum, which will maximize our modal gain. We now begin the design by optimizing the waveguide thickness and width. The bottom of the waveguide is made of HSQ, with a refractive index of ~ 1.42. The top layer is comprised mainly of Alq3, and so we approximate
the refractive index to be 1.7. The thickness of the HSQ layer is determined by several factors. If it is too thin, the waveguide will not survive the etching and evaporation processes. If it is too thick, it will increase the number of modes in the waveguide, increasing the lasing threshold of any given mode. We set the thickness of the HSQ to 150 nm. The thickness of the Alq3:DCM layer is then determined by increasing the thickness to confine the mode and raise its effective index, but to not introduce any order modes by increasing it too much. The value we choose is 150 nm. Similarly the width of the waveguide needs to be wide enough to allow for a relatively large index contrast between the holes and the dielectric after we introduce the photonic crystal, but the width should not be so wide that it introduces additional guided modes. We set the waveguide width to be 440 nm. Figure 4-3 shows the mode profile of the waveguide mode.

Now that we have two dimensional confinement of the light in the waveguide, we need to introduce a photonic crystal to control the modes along the waveguide. To lower our threshold as much as possible, we will want to keep the number of modes to a minimum, so our first task is to create a photonic bandgap centered around the lasing frequency. Later we will introduce a localized defect mode in the center of the bandgap which will be the lasing mode. To guide our design, we recall some of the key points from chapter 3. The index contrast determines the size of the bandgap. The frequency of the bands depend to a large degree on the lattice constant, but also on the size of the holes relative to the unit cell size. Because we are working with low index materials such as HSQ and organics, we can use elliptical holes instead of...
Figure 4-3: The mode profile is plotted showing the regions of the waveguide that correspond to organic material and HSQ.

circular holes to increase the index contrast between the waveguide region and the holey region. We begin by tweaking the lattice constant $a$ as well as the radii to create a large bandgap centered around our target frequency. We choose a lattice constant of $a = 270$ nm and for the holes $r_1 = 65$ nm and $r_2 = 150$ nm, where $r_1$ is the radius along or parallel to the waveguide and $r_2$ is the radius perpendicular to the waveguide.

We now have created a nanobeam photonic crystal, but we need to create a cavity by introducing a defect mode, otherwise we will just had a band-edge laser, which will have a high mode volume. To create a cavity, we change the the size and periodicity of the center holes to shift the dielectric band-edge to be of the target frequency. We need to increase the frequency of the bands, so we decrease the lattice constant to
\( a = 226.8 \) nm and the radii to \( r_1 = 54.6 \) nm and \( r_2 = 126 \) nm.

Though we have introduced a defect mode, we can improve the quality factor of the mode by tapering the size and the periodicity of the holes linearly to create a smoother transition from the region that the lasing mode exists to the region that it is in the photonic bandgap. By smearing the mode over several holes, we increase its spatial distribution, which means in reciprocal space it will have a narrower distribution. This type of momentum space consideration is commonly seen in the literature\(^{[30]}\)\(^{[31]}\). The reason for the higher quality factor is that with a small distribution in reciprocal space, less of the mode will overlap with the light cone, meaning less light will couple into lossy radiation modes. By making this taper slower by increasing the number of tapered holes, we increase the quality factor dramatically.

Finally, to make the cavity have a radiation limited \( Q \), so that the light is easier to collect from an objective, additional holes were added to the ends of the tapered holes to increase the reflection of the cavity mode at the interface between tapered holes and non-tapered holes. These end holes, we call mirror holes, as they function to confine the cavity mode by creating Bragg mirrors at both ends of the cavity. The lattice constant of these holes and the radii are fixed at \( a = 270 \) nm, \( r_1 = 65 \) nm, and \( r_2 = 150 \) nm. Even with low index contrast system, the \( Q \) of these cavities can be designed to be over a million by using a large number of holes. However, as we will discuss later, the roughness of the organic layer causes cavity modes to scatter into radiation modes, and ultimately this limits our \( Q \). Therefore, the design we report the results for is formed by 6 tapered holes and 10 mirror holes on the ends, and this design has a theoretical \( Q \) of about 10,000. Figure 4-4 shows a plot of the y component of the electric field of the cavity mode. We plot the y component as the mode is a TE-like mode, and the electric field points mostly in the y direction.

4.3 Fabrication

Figure 4-5 shows a summary of the fabrication steps. We begin fabrication of the devices by dicing our silicon substrate. We do a particle clean by sonicating the
pieces first in acetone and then in isopropanol, each for 5 minutes. We then clean the substrates of any residual organic molecules in a piranha bath for 10 minutes. We mix piranha by adding 1 part hydrogen peroxide with 3 parts sulfuric acid. The substrates are then rinsed with deionized water and dried with a nitrogen gun. Finally, the substrates are baked for 20 minutes at 180° C to evaporate any moisture left on the substrate. The pieces are now clean and ready for processing. We begin processing by spincoating a layer of 6% concentration Dow Corning XR-1541-4 E-Beam Resist, commonly known as HSQ, at 2000 rpm for 50 seconds. The substrates are then baked for 5 minutes at 90° C to remove any excess solvent. The substrates are now ready for patterning. Using an Elionix ELS-F125 ebeam writer, we pattern our photonic crystal cavities at 125 kV. The dosages we use for our patterns are 3200, 3520, and 3840 μC/cm², while we write support structures for the purpose of anchoring the waveguides at a dosage of 960 and 1280 μC/cm². The support structures are much larger than the waveguides, and because of the proximity effect, they require lower dosages than the photonic crystal patterns. The reason for using multiple dosages for our devices is that the HSQ resist has an effective shelf life of around 3 months. As it ages, it self-develops, requiring smaller dosages to be developed. Figure 4-6 shows an undercut structure that has been overexposed. To compensate for the constantly changing dosage required, we use several dosages each time we fabricate a device. After electron beam lithography, the substrates are developed for 14 seconds in an aqueous solution of 25% concentration tetramethylammonium hydroxide (TMAH), rinsed in deionized water, and dried using nitrogen guns. The samples then undergo
rapid thermal annealing at 600, 700, and 800° C for 60 seconds in a nitrogen rich environment. The purpose of annealing these samples is to relieve stress in the HSQ layer by the removal of Si-H bonds [32]. The importance of this step is emphasized in Figure 4-7, which shows the results of completed devices that did not include this annealing step during their fabrication. Without annealing the HSQ, the stress in the waveguide causes it to break once it is undercut during the etch step.

We now have a nanobeam photonic crystal cavity that we undercut by etching with XeF₂ gas. The XeF₂ etch is a purely chemical etch, is isotropic, and has a selectivity of 1000:1 for Si : SiO₂. The etcher we use does not use a mass flow controller, so the etch times are somewhat variable, but the average etch usually consists of 2-3 60 second cycles. After etching, the structure is ready for incorporation with the organics. The devices are loaded into a thermal evaporator where a thin layer of Alq₃:DCM is
Figure 4-6: The overexposure of HSQ is evident from the filled in holes in the photonic crystal.

Figure 4-7: SEM images shows the effect of annealing on devices. In (a) we see that without annealing, many of the devices are broken, and in (b) a device that has been annealed was successfully fabricated.

deposited coating the entire surface of the sample. The suspended waveguide region forms a structure analogous to a shadow mask, but instead of having the purpose of masking a region on the surface of the substrate, the suspended region builds up a
film of organics on top of it, separating it from the rest of the sample, and forming a cavity. Figure 4-8 shows SEM images taken of complete devices. The devices are now complete and can be characterized. However, since organic molecules are known for photobleaching in oxygen rich environments (such as air), we package our devices in a nitrogen environment, by sandwiching them between 2 glass microscope cover slips and sealing them with vacuum epoxy (TorrSeal).

4.4 Characterization

To measure our lasers, we use a pulsed laser source. Our system uses a mode-locked titanium sapphire laser to seed a regenerative amplifier, generating high power pulses. These pulses pump an optical parametric amplifier, and at the output we get 100 fs pulses centered around 400 nm at a repetition rate of 1 kHz. The beam is expanded and passed through an iris, removing the tails of the beam so that the intensity profile of the beam is near uniform. The pump light intensity is adjusted by rotating a variable neutral density filter. The beam is focused onto our sample using a 50X objective down to a spot size of 11 μm. The uniform intensity profile generates a uniform excitation density in the sample. The collected laser light passes through a
dichroic and bandpass filter before being coupled into a multimode fiber and sent to a spectrometer for analysis (Princeton Instruments SpectraPro). Figure 4-9 shows a schematic of the experimental setup.

Figure 4-9: The samples are characterized by the setup shown. Input pulses are expanded and clipped to achieve a flat intensity profile. The pump laser light is spectrally filtered from the collected laser light. The device emission is analyzed on a spectrometer.

We observe the characteristics of lasing from pumping our devices. As we increase the pump intensity, we observe a lasing threshold of the cavity mode at 618.5 nm that corresponds to an input absorbed pulse energy density of $4.2 \, \mu J/cm^2$. We observe a collapse of the linewidth of the lasing mode down to $0.14 \, \text{nm}$, which is the lower limit of the spectrometer. The emission from the mode is highly polarized. Figure 4-10 shows the data from optical characterization of these devices: the output intensity as well as the linewidth of the lasing mode as a function of input absorbed pulse energy density, and the spectrum of the emission below and above threshold.

4.5 Modeling

Lasing in an Alq3:DCM film can be modeled using a simple 4-level system [33][34]. We label $N_{Alq3}$ the excited state density in the LUMO of Alq3, $N_{DCM}$ the density
(a) Intensity and linewidth as a function of input energy density

Figure 4-10: Through optical characterization of our devices, we see the signatures of lasing. (a) We see a characteristic threshold in the intensity as a function of input absorbed energy density. We also see linewidth narrowing of the lasing mode, down to the limit of our spectrometer. (b) We observe lasing through a distinct cavity mode.

of the LUMO of DCM, and \( N_p \) the photon density of the lasing mode. We pump the system using a ultrafast laser pulses \( \sim 100 \) fs long which we can treat as delta functions. Since the Alq3 absorption and DCM emission are spectrally separated, and the excited state lifetime is much shorter than the inverse of the laser repetition rate, the probability of exciting Alq3 after a laser pulse has arrived is negligible. To model the dynamics, we only need to consider the excited states of Alq3 and DCM as well as the photon density of the lasing mode. We cast our equations in a form similar to the two level system equations (equation 2.31):

\[
\begin{align*}
\frac{d}{dt} N_{Alq3}(t) &= \frac{P_{pump}(t)}{A_{sp}h\nu} \frac{\eta_{abs}}{t_{active}} - \frac{N_{Alq3}(t)}{\tau_{rad}} - \frac{N_{Alq3}(t)}{\tau_{nr}} - \frac{N_{Alq3}(t)}{\tau_{FRET}} \\
\frac{d}{dt} N_{DCM}(t) &= \frac{N_{Alq3}(t)}{\tau_{FRET}} - v_g \sigma_{SE} N_{DCM}(t) N_p(t) - \frac{F_m v_g \sigma_{SE} N_{DCM}(t)}{V_{eff}} \\
&\quad - \frac{F_s v_g \sigma_{SE} N_{DCM}(t)}{V_{eff}} \frac{N_{DCM}(t)}{\tau_{nr}} \\
\frac{d}{dt} N_p(t) &= v_g \Gamma \sigma_{SE} N_{DCM}(t) N_p(t) + \frac{F_m v_g \Gamma \sigma_{SE} N_{DCM}(t)}{V_{eff}} - \frac{N_p(t)}{\tau_{cavity}} \tag{4.1}
\end{align*}
\]

\( P_{pump}(t) \) is a train of 100 femtosecond pulses at a repetition rate of 1 kHz so we can simply approximate it by a delta function, and divide the average power by the number of pulses to get the power per pulse. We divide by the photon energy and
the area of the spot to get the photon flux per pulse. Dividing by the thickness and 
multiplying by the absorbed fraction of the light gives us the exciton density generated 
by the pump in the organic material. The other three terms in the top equation 
correspond to the radiative, non-radiative, and FRET decay pathways of the excitons 
in Alq3, with lifetimes \( \frac{1}{\tau_{\text{rad}+\text{nr}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{nr}}} = (16 \text{ ns})^{-1} \) \cite{35} and \( \tau_{\text{FRET}} = 10 \text{ ps} \) \cite{36}. We 
set the group velocity of the lasing mode \( v_g = c/n_{\text{eff}} \), where \( n_{\text{eff}} \approx 1.33 \) is the effective 
index of the mode. The confinement factor is defined as \( \Gamma = \frac{\int_{E>0} E^2 \, dV}{\int_{E>0} \, dV} = 0.5 \) 
which we calculate by FDTD simulations, and \( \sigma_{SE} \) is the stimulated emission cross 
section of DCM at the lasing frequency, which we take to be \( 1.1 \times 10^{-16} \text{ cm}^2 \). The 
Purcell enhancement of the mode \( F_m \) and \( \beta \), inside the factor account for other 
modes of spontaneous emission \( F_s \equiv F_m \frac{1-\beta}{\beta} \), are used as fitting parameters. Finally, 
the lifetime of the cavity is given by \( \tau_{\text{cavity}} = \frac{Q}{2\pi \nu} \), where \( Q \) is the quality factor of 
the mode, and \( \nu \) is the frequency of the lasing mode. We extract a quality factor of 
\( Q = 3600 \) by measuring the line width of the cavity mode, just before lasing.

We reduce the equations 4.1 to steady state so that we can compare the model 
with our measured input/output characteristics:

\[
0 = \frac{P_{\text{average}} \eta_{\text{abs}}}{\int_{E>0} E \, dV} \cdot \frac{\tau_{\text{rad}+\text{nr}}}{\tau_{\text{rad}+\text{nr}} + \tau_{\text{FRET}}} - v_g \sigma_{SE} N_{\text{DCM}} N_p(t) - \frac{F_m v_g \sigma_{SE} N_{\text{DCM}}}{V_{\text{eff}}}
\]

\[
0 = v_g \Gamma \sigma_{SE} N_{\text{DCM}} N_p + \frac{F_m v_g \Gamma \sigma_{SE} N_{\text{DCM}}}{V_{\text{eff}}} - \frac{N_p}{\tau_{\text{cavity}}}
\]

(4.2)

We find an optimal fit between our data and model for \( \beta = 0.017 \) and \( F_m = 2.6 \). 
Figure 4-11 shows the model we fit to our data to extract these parameters.

4.6 Discussion

The value of \( \beta \) for our nanobeam lasers is much lower than values reported in the 
literature for lasers using similar cavities\cite{21}, which approach unity. Our lower value
Figure 4-11: The steady state model of lasing shows a good fit to our data.

is explained by the low index contrast of our system, with a higher radiation loss due to the low confinement of the mode compared to higher index contrast systems. Our $\beta$ is still 2 orders of magnitude higher than a traditional VCSEL structure, which leads to the low threshold, despite a surface roughness limited $Q$ that is comparable to $Q$'s of a VCSEL. The rather modest Purcell enhancement of $F_m = 2.6$ is surprising, but reasonable considering the large inhomogeneous broadening of the organic light emitters.

The far field emission profile of our lasers is shown in figure 4-12a. We would expect the emission of the cavity mode to look like a dipole, yet we measured it to be a quadrapole. The explanation for this relies on multipole expansion theory, which states that the light emitted from a device can be expanded as a sum of a dipole, a quadrapole, a hexapole, etc. By designing the cavity to have a high $Q$, we create a far field profile from the device where the dominant radiation term, the dipole term, is canceled by destructive interference. To confirm this, we compare the emission from the optimally designed device with a suboptimal design, shown in figure 4-12b. As we suspect, the suboptimal device shows a dipole far field emission...
profile. It also has a lasing threshold that is more than an order of magnitude higher. The multipole expansion theory helps us to understand the correlation between high quality factor and far field emission profile, as we observe with our lasers.

![Emission Profiles](image)

Figure 4-12: We notice that the emission profile (a) of our optimal device is a quadrapole, which is explained by the multipole cancellation theory. We measure the emission from a suboptimal device (b) and find that it looks like a dipole.

### 4.7 Conclusion

We demonstrate a low threshold organic laser using a nanobeam photonic crystal cavity. This structure uses a high Q/V ratio and high spontaneous emission factor to reduce the lasing threshold. The quality factor of the device is limited by the surface roughness of the organic layer, and could be increased by improving the thermal deposition process.
Chapter 5

Quantum Dot Nanobeam Lasers

Organic lasers address the need for a low threshold visible laser that is tunable by changing the dye and tweaking cavity parameters. However, we showed that even by designing an organic laser with a high Q/V ratio, their performance is limited by fabrication challenges. Even if these challenges are eventually overcome, the dark long-lived triplet excitonic states make continuous wave operation and electrical pumping of these devices very difficult.

With quantum dots, we avoid many of the fundamental shortcomings of organic molecules related to their dark states. As we have discussed, the surface of quantum dots is passivated by organic ligands that can be functionalized with different chemical groups to adjust the bulk electronic and optical properties of a quantum dot film. The passivation of these surface states also gives QDs remarkable stability in air environments, which may lead to more robust lasers.

5.1 Practical Considerations

We use a design similar to that of the organic laser, but rather than having to separate the waveguide and gain layers because of the fabrication, we can mix the quantum dots into a polymer matrix to form a composite waveguide/gain structure. Not only does this design simplify the fabrication process, but it now forms an additional symmetry plane along the waveguide that allows us simplify our simulations. We can
now take advantage of the full mirror symmetry of the waveguide along all 3 axes, and this provides a significant speedup to our simulations.

The bulk refractive index of a quantum dot film using CdSe/Cd$_{0.5}$Zn$_{0.5}$S is 1.7, but we will assume that the fraction of dots is low compared to the polymer matrix in which the dots are embedded. We want to select a positive tone ebeam resist to embed the dots into, so that their exposure to high energy electrons is minimized. The two best candidates for this are PMMA and ZEP, which have refractive indices of $\sim 1.48$ and 1.55 respectively. Both ebeam resists can be used to make high resolution features, so ZEP would be more desirable due to its higher index. However, ZEP comes dissolved in anisole, a solvent that is chemically incompatible with the ligands on the quantum dots. For this reason, we select PMMA dissolved in chlorobenzene as our ebeam resist.

Previously we probed the organic laser by illuminating the waveguide from the top, and collecting light through the same objective. Though we designed a radiation limited cavity, most of the emitted light was outside of the collection cone of our objective, which reduced our signal to noise ratio. For this cavity, we will design it to have a high quality factor, but also to have high transmission through the waveguide, so that we can collect light through the ends of the waveguide instead of using the objective. Figure 5-1 shows a schematic of our QD lasers.

![Figure 5-1: The quantum dot laser cavities are designed to emit through the waveguide, increasing the collection efficiency of laser emission.](image-url)
5.2 Design

In the previous design, the holes were largest at the edges and smallest in the center. If we try to couple light in through the waveguide, there will be a large impedance mismatch at the interface of the unpatterned waveguide and first hole, which will result in light being reflected at the interface. To minimize this reflection, we will reverse the pattern of the holes, so that the smallest holes are near the edges and largest are in the center. In addition to using a taper in the center to confine the cavity mode, we can taper the mirrors near the edges of the waveguide to slowly "turn on" the photonic crystal, which will minimize reflected light. Finally, we consider that our tapers before included changing the lattice spacing. To minimize reflections along the waveguide, we will keep the lattice constant the same.

We select our target frequency for the lasing mode to be 476 THz, near the peak of the quantum dot emission spectrum. The design begins as before by optimizing the thickness and width of the waveguide, to achieve a relatively high effective refractive index of the mode of the lowest order mode, while minimizing the number of higher order guided modes. We assume that the fraction of dots will be small, so the refractive index of the waveguide is approximated as 1.48, the index of PMMA. We choose a waveguide thickness of 150 nm, and a waveguide width of 750 nm. Figure 5-2

The photonic crystal design we use is adapted from the literature[37][38] to provide high transmission along the waveguide as well as high quality factor, and differs slightly from the design we used with the organic laser.

Rather than considering how to open a bandgap first, we consider the cavity mode. We optimize the hole spacing and radii to give us a large band gap with the dielectric band-edge mode corresponding to the emission peak of our quantum dots. We set the hole periodicity \( a = 282 \) nm. The center elliptical holes have radii \( r_1 = 75 \) nm and \( r_2 = 360 \) nm. We taper the hole size to a smaller size, which pushes the bands down, forcing the cavity mode into the gap. While we tapered all the dimensions linearly with the last design, here we carefully consider the rate at which the taper is applied,
to optimize the quality factor. In the literature, it has been shown that an optimal field profile is a Gaussian[31], and that a Gaussian field profile can be achieved by a quadratic taper of the filling fraction of the holes[37][38], which is the fraction of the volume of a hole per unit cell. For our design, we achieve a quadratic taper by linearly tapering both radii of our holes. We optimize the final radii to maximize the quality factor and find final radii of $r_1 = 67$ nm and $r_2 = 321.6$ nm.

A Q of 500,000 is easily achieved by increasing the number of tapered holes and mirror holes to 50 each, but we limit the tapers to 18 and mirrors to 20 to achieve a modest Q of 10,000. Figure 5-3 shows the electric field profile of the cavity mode. The astute reader might remember that the organic laser design only required 6 tapers and 10 mirrors to achieve the same Q, but this is due to the higher index contrast.
compared to this system, with the mode being confined in organic layers with an
index of 1.7 compared to our polymer waveguide with an index of 1.48. Nevertheless,
a high theoretical Q is achievable by increasing the number of holes.

Figure 5-3: The y component of the electric field for the cavity mode is plotted.

5.3 Fabrication

Before fabricating devices, we need to make a solution of QDs and PMMA to be used
later for spincoating. We use a solution of proprietary CdSe/Cd$_{0.5}$Zn$_{0.5}$S quantum
dots dissolved in toluene, provided to us by QD Vision. We induce flocculation of
the QDs by slowly adding IPA to the solution of QDs in toluene. When the initially
transparent solution becomes cloudy, it is centrifuged for 3 min at 3600 rpm, and
the supernatant solution is dumped out, leaving only a pellet of quantum dots at the
bottom of the vial. To redisperse the quantum dots, we add Micro Chem 950PMMA
C 2% ebeam resist, and then sonicate the solution for several hours. For the devices
shown, the ratio of PMMA/QDs by weight was about 4/1.

Figure 5-4 shows a summary of the fabrication steps of a QD nanobeam laser. To
begin fabrication of our devices, we dice and clean silicon wafers as we did for the
organic lasers. We spincoat the PMMA-QD solution for 5 seconds at 500 rpm and then
45 seconds at 3000 rpm. The devices are then baked for 1 minute at 180 °C to remove
excess solvent. The devices are now ready for patterning. Using an Elionix ELS-
F125 ebeam writer, we pattern our photonic crystal cavities at 125 kV. Like with the
organic cavities, we write devices at different dosages, to find the optimal dosage. For
the quantum dot cavities, we use dosages of 480 and 640 μC/cm$^2$. After patterning,
the devices are developed by immersion in a 1:3 methyl butyl isoketone:isopronanol
solution for 60 seconds followed by an isopropanol rinse and dried with a nitrogen gun. The last step for the devices is to undercut them by etching with XeF₂ gas. We have found using the tool available to us that 30 seconds gives good results. The devices are now complete and ready for testing. Unlike the organic devices, they do not need to be packaged as the quantum dots are photostable in air.

Figure 5-4: Summary of steps for fabrication of QD nanobeam lasers.

5.4 Characterization

Before testing the devices, we want to confirm that we actually have photonic crystal cavities. We made the assumption that the PMMA-QD film would behave in the same way as a pure PMMA film would, and we need to confirm our assumptions. The devices are mostly made of PMMA, which charges in an SEM and reflows when the beam is tightly focused. Therefore, getting good images of the photonic crystal structure is challenging. We resort to other methods of characterizing the devices.
first, beginning with optical characterization. We illuminate the structure using the setup described for the organic cavities to look for cavity modes, but we do not see them. In fact, as we move the sample stage around under the microscope, we see brighter and darker spots, suggesting that the dots are not uniformly mixed.

We decide to investigate the surface using atomic force microscopy (AFM). We take AFM images of the surface of our PMMA/QD film and compare it with a film of just PMMA. Figure 5-5 shows the comparison between the surfaces of the two films. We observe that the surface of the PMMA/QD film shows features that appear to be densely packed quantum dots. The feature sizes match those of single quantum dots, and the height differences between islands of features suggest that there are several stacked monolayers of QDs. These AFM images show that the quantum dots have phase separated to the surface of the PMMA film. Figure 5-6 shows the topography of a 1 μm × 1 μm square. A trace is drawn in figure 5-6a with its corresponding height profile displayed in figure 5-6b.

We saw that the films of PMMA/QD mixtures were not homogeneous and resulted in phase separation of the dots from the PMMA. This process is commonly seen using quantum dots dissolved in many different solvents, with a variety of other matrix materials[39]. Though the roughness of the film would likely not allow for us to build high quality laser cavities, we decided to try fabricating devices to possibly see
Figure 5-6: Atomic force microscopy of the surface of our PMMA/QD film suggests the phase separation of the QDs to the top of the PMMA. (a) Topography of a 1 μm x 1 μm square (b) Height profile of the trace shown in (a) with dashed lines suggesting monolayers of QDs

spectral signatures of cavity modes from the photoluminescence spectrum. In addition to fabricating cavities with our phase separated films, we tried also fabricating devices where the PMMA layer and QD layer were deposited by separate spin coating steps. With one device we tried spincoating on top of patterned PMMA layers, followed by developing. With another, we tried developing the patterned PMMA layers, and then spincoating QDs on top. These devices were measured using the same experimental setup used for characterizing the organic lasers. No photoluminescence was observed from the device that had been developed before spincoating QDs. The devices that had QDs deposited before developing showed only weak photoluminescence from the waveguide regions, and none from the rest of the bulk film. However, no cavity modes were observed in their spectrum. The cavities fabricated using phase separated films were broken.
Chapter 6

Concluding Remarks

We demonstrated nanobeam photonic crystal lasers using Alq3:DCM, and achieved a low threshold of 4.2 μJ/cm². Lower thresholds could be achieved by improving the fabrication process. We showed that the high quality factor could be interpreted using multipole cancellation theory. Our lasers are a proof of concept for the technique of designing nanobeam photonic crystal lasers for the visible spectrum independent of concerns with lattice matching or bandgap. The emission wavelength of the lasers can be tuned by simply adjusting geometric parameters, and by choosing a different organic material.

We also designed a laser cavity that uses CdSe/Cd0.5Zn0.5S quantum dots for gain. These dots can have their emission spectrum altered by adjusting their size, and they also allow for the design of visible lasers using a material set that covers the entire visible spectrum. Though we did not successfully fabricate photonic crystal cavities, the project is ongoing.

6.1 Future Project Plans

The design we used for the organic laser was successful, however we need to lower the threshold substantially if we want to make any progress towards achieving CW operation or electrical pumping. Our design showed that the mode was confined primarily to the organic layer, which was lossy due to surface roughness. If we instead
confined the mode to the HSQ waveguide, which should be much smoother due to the viscous reflow achieved by rapid thermal annealing, and overlap only a small portion of the mode with the organic material, the laser threshold could perhaps be lowered. Though the gain would be reduced by a smaller confinement factor, the reduced scattering into radiation modes could possibly raise the quality factor closer to the theoretical limit of around $10^6$.

The quantum dot laser project is ongoing and we are investigating ways to incorporate the QDs into a PMMA matrix without phase separation. A recent paper shows large area composites of PMMA/QDs for solar applications[40]. In their paper, they discuss the use of QDs that have been functionalized with monomers and are then polymerized by the use of thermal radical initiation. We also are looking into the use of free radicals to initiate polymerization of monomers attached to QDs.

In addition to the investigation of creating PMMA/QD composite materials, we are considering the use of inverted structures, where the PMMA layer is patterned in the exact inverse of before, to create a negative of the photonic crystal pattern. The exposed region is developed leaving behind a hole that we can then fill in with quantum dots. Though the index contrast will not be as high as the suspended nanobeam cavities, the fabrication of such cavities is simpler, and the quality factor can be increased by simply adding more holes to the cavities. This approach using nanobeams that are not suspended may prove to be a more viable approach to creating nanobeam photonic crystal lasers with quantum dots.


