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Colloidal Quantum Dot Based Photonic Circuits and Devices

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Colloidal Quantum Dot Based Photonic Circuits and Devices

by

Nicky E. Okoye

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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THE CITY UNIVERSITY OF NEW YORK
Abstract

Colloidal Quantum Dot Based Photonic Circuits and Devices

by

Nicky E. Okoye

Adviser: Dr. Vinod M. Menon

Colloidal quantum dots have desirable optical properties which can be exploited to realize a variety of photonic devices and functionalities. However, colloidal dots have not had a pervasive utility in photonic devices because of the absence of patterning methods. The electronic chip industry is highly successful due to the well-established lithographic procedures. In this thesis we borrow ideas from the semiconductor industry to develop lithographic techniques that can be used to pattern colloidal quantum dots while ensuring that the optical properties of the quantum dots are not affected by the process. In this thesis we have developed colloidal quantum dot based waveguide structures for amplification and switching applications for all-optical signal processing. We have also developed colloidal quantum dot based light emitting diodes.

We successfully introduced CdSe/ZnS quantum dots into a UV curable photo-resist, which was then patterned to realize active devices. In addition, “passive” devices (devices without quantum dots) were integrated to “active” devices via waveguide couplers. Use of photo-resist devices offers two distinct advantages. First, they have low scattering loss and secondly, they allow good fiber to waveguide coupling efficiency due to the low refractive index which allows for large waveguide cross-sections while supporting single mode operation. Practical planar photonic devices and circuits incorporating both active and passive structures can now be realized, now that we have
patterning capabilities of quantum dots while maintaining the original optical attributes of the system.

In addition to the photo-resist host, we also explored the incorporation of colloidal quantum dots into a dielectric silicon dioxide and silicon nitride one-dimensional microcavity structures using low temperature plasma enhanced chemical vapor deposition. This material system can be used to realize microcavity light emitting diodes that can be realized on any substrate. As a proof of concept demonstration we show a 1550 nm emitting all-dielectric vertical cavity structure embedded with PbS quantum dots. Enhancement in spontaneous emission from the dots embedded in the microcavity is also demonstrated.
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Chapter 1

Colloidal Quantum Dot Background

Quantum dots are crystal structures with radii on the order of several billionth of a meter. They contain hundreds to hundreds of thousands of atoms. The bound states of quantum dots are widely spaced similarly to atoms. The density of states is a delta function unlike a bulk semiconductor which exhibits a continuous function. In addition, the quantum dots are nanocrystals that exhibit translation invariance but only within a finite space. Like solid crystals, nanocrystals demonstrate energy gap attributes. The energy gap is between the supremum of occupied molecular orbital states (HOMO) and the infimum of unoccupied molecular orbital states (LUMO) (Figure 1.1). In appendix A, a computational approach using the variational method is implemented to solve for the ground state of the nanocrystal in a one electron approximation. This illustrates the origin of the energy gap found in these nanocrystals.

Figure 1.1. This is a generic representation of the energy gap between the LUMO and HOMO states. The gap (not drawn to scale) is considerably larger than the spacing between the lower states and the spacing between the higher states. Also note one may encounter other gaps as one moves higher up in energy.
Within this framework, the ground state of the system consists of the lower states filled by electrons up to the HOMO state. An electron may be excited into an unoccupied LUMO state or higher. The result is a hole with opposite charge in one of the lower states. There are also excitations that form excitons. However, these are excitations of the crystal involving transitions of electrons from the filled ground state to a state that resides within the gap as shown in figure 1.2.

Figure 1.2. As in figure 1.1 the filled ground state with empty excited states is shown. However, there are now “forbidden” states within the HOMO-LUMO gap. The energy gap is denoted as $E_G$. $E$ designates the exciton energy with magnitude corresponding to the green arrow from the HOMO state to one of the states within the gap. The different $N$ states refer to the different exciton states.

Energy states within the gap are forbidden within the original framework. Analysis of collective excitations \[1\], demonstrate transitions from the ground state to forbidden
energy states. Such excitations may be described by as a coulomb interaction between a hole and an electron. The reduced mass of the effective masses of the electron and hole gives the mass of the exciton where the binding energy is the difference between the energy state within the gap and the energy gap. Figure 1.2 illustrates the hydrogen like bound states that approach the LUMO state. In this Wannier model, the Hamiltonian may be written as

\[
\hat{H} = \left( \frac{\hbar^2 \nabla^2}{2\mu_{ex}} \right) - \left( \frac{e^2}{\varepsilon r} \right)
\]

(1.1)

The mass of the exciton is denoted by \( \mu_{ex} \) and \( \varepsilon \) is the permittivity of nanocrystals, \( e \) is the charge of the electron and \( r \) is the Bohr radius which corresponds to the distance between the electron and the hole. However, as shown by Brus [2], the exciton in the nanocrystal has additional contributions to the total energy that is dependent on the size of the nanocrystals and its permittivity. This is due to the polarization effects on the electron and hole charges inside the crystal. When the size of the nanocrystal is much larger than the exciton Bohr radius then the Wannier model is a good approximation. However as the size of the crystal becomes smaller than the exciton Bohr radius then quantum confinement has a larger contribution to the bound energy states than the coulomb interaction. The confinement term may be evaluated for s-orbitals by evaluating the Hamiltonian with respect to the spherical Bessel functions with angular momentum 0. The confinement term for the binding energy of an s-orbital state may then be expressed as

\[
\frac{\hbar^2 n^2 \pi^2}{2\mu_{ex} R^2}
\]

where \( R \) is the radius of the nanocrystal and \( n \) is an integer that corresponds to the particular energy state. Assuming the potential of the Hamiltonian is infinite outside the extent of the nanocrystal volume, the wave function must be zero outside the
structure and hence the boundary of the crystal must be a nodal surface for the wavefunction. Hence an evaluation of the spherical Bessel function at the surface must correspond to an evaluation of a “zero”. In other words \( j_l\left(\frac{2\mu_{ex} (E-E_G)}{\hbar} R\right) = 0 \). Since the states under investigation are s-orbitals, the spherical Bessel function must have the form

\[
\frac{\sin\left(\frac{n\pi r}{R}\right)}{r}
\]

where \( n \) is a positive integer and \( r \leq R \) and the binding energy is \( E-E_G \). The binding energies corresponded to bound states of the exciton. The negative of these energies are the ionization energies to promote an electron bound to the hole to a free carrier. In doing the confinement analysis the energy is still measured with respect to the energy gap. The energy states with respect to the energy gap may be expressed as

\[
E - E_G = \left(\frac{\hbar^2 n^2 \pi^2}{2R^2}\right) \left[\frac{1}{m_e} + \frac{1}{m_h}\right]
\]

(1.2)

\( m_e \) is the effective mass of the electron and \( m_h \) is the effective mass of the hole. Looking at this confinement term alone, it is evident that the system resembles that of a non-interacting electron-hole pair quantum mechanically confined to a sphere smaller than the exciton Bohr radius. Hence, the term “quantum dot” aptly describes the system. It is an artificial atom in that it is spherically symmetric and has wider spaced energies. Now we rewrite equation (1.2) as

\[
E = \left(\frac{\hbar^2 n^2 \pi^2}{2R^2}\right) \left[\frac{1}{m_e} + \frac{1}{m_h}\right] + E_G
\]

(1.3)

Recall within the HOMO-LUMO system, the energy gap is the activation energy needed to excite an electron from the ground state to the HOMO state. The activation energy in the confined system would then be
Equation 1.4 may then interpreted as the energy gap of the quantum dot.

Since the energy gap of the quantum dot is now a function of the radius, its absorption spectrum can be tuned by varying the dot size. The larger the size, the smaller the energy needed to create a non-interacting electron-hole pair. Smaller energies required for excitation correlates to absorption at longer wavelengths. The smaller the size the greater the energy needed for electron-hole creation requiring absorption at shorter wavelengths. This is illustrated in figure 1.3.

\[
\left( \frac{\hbar^2 n^2 \pi^2}{2R^2} \right) \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] + E_G
\]  

(1.4)

Figure 1.3. Absorption spectra for different sized CdSe/ZnS. The shift from the blue absorption spectra to the orange absorption spectra is an increase in quantum dot size from blue to orange. [Figures from the website of Evident Technologies, www.evidenttech.com.]
When the quantum dots of a given size and chemical constitution are excited by a given wavelength, the excited electrons then “relax” to their initial state. During the relaxation period, the electron may decay to a state lower than its excited state with accompanied emission of electromagnetic radiation of longer wavelength than the excitation wavelength. Following this, there will be an intersub-level transition from this lower state to the initial state which would involve non-radiative decay. This results in a shift in the emission maximum from the absorption maximum often referred to as the Stokes effect as illustrated in figure 1.4.

Figure 1.4. These are absorption and emission spectra of PbS quantum dots distributed by Evident Technologies. Absorption spectrum is for one size of dots emitting at about 1420nm and emitting at about 1350 nm. Observe how the emission is Stokes shifted from wavelength of absorption.
The quantum dots illustrated in previous figures are colloidal suspensions in an alkane or aromatic solvent. In order to achieve this solubility, the quantum dots must be encapsulated in a set of compounds referred to as ligands. Figure 1.5 gives a visual representation of such a system. The ligands keep the quantum dots separate from one another as well as make them soluble in the given solvent.

Figure 1.5. A coordination complex is formed with the nanocrystal quantum dot as the center “atom”. The functional groups or ligands are trioctylphosphine oxide and trioctylphosphine (not shown) molecules that cap the nanocrystal.

The result is a solution with tunable absorption and photoluminescence. Also, it has spectral properties exhibiting low optical power thresholds for absorption saturation, amplification and fast recovery times for switching in photonic circuits. These photonic circuits can be used in telecommunication systems where optical to electrical and electrical to optical conversion procedures are unwarranted. Colloidal quantum dots also
allow thin film deposition processes; have self-assembly attributes, and adhesion to silicon and many other substrates that are compatible within the integrated chip fabricating architecture. In addition, using colloidal quantum dots provides unprecedented flexibility in the choice of substrates unlike quantum dots grown using molecular beam epitaxy (MBE). In the latter case with the Stranski-Krastanov, (SK), method where quantum dots are grown using MBE, the quantum dots are set in place usually on InP or GaAs substrates. Furthermore, there are only a few applications of SK quantum dots emitting in the 1550 nm wavelength range. Such applications have been on substrates of InP cleaved along the (311) plane [3] as opposed to silicon substrates. Also, the chemistry in synthesizing colloidal quantum dots gives a range of wavelengths for a given compound (figure 1.3). This gives more tolerance in designing and fabricating a photonic device that has a compound specific requirement.

Besides the standard semiconductor materials, more recently there have been demonstrations of light emitting devices utilizing organic materials and inorganic nanocrystals on solid and flexible substrates [4, 5]. There have also been demonstrations of lasing using self-assembled block copolymers, co-extrusion of two polymers and spin coating for Distributed Bragg Reflector and Distributed Feedback lasing in organic medium [6-13]. Colloidal quantum dots also exhibit lasing when incorporated into microcavity geometries such as microspheres, distributed feedback structures, cylindrical cavities, and micro rings [14-19].
Chapter 2

Colloidal Quantum Dot Based Amplifier and Switch

2.1 Motivation

Colloidal quantum dots have highly desirable photonic properties such as high luminescence yield, wavelength scalability and photo stability. However, the solution state of their host renders them incompatible for fabricating photonic structures such as waveguides. There is no well-established technique that incorporates quantum dots into transparent host matrices without affecting their optical properties [20-22]. It is desirable to incorporate colloidal quantum dots as the active medium to produce photonic integrated circuits on silicon which would cover a wide range of wavelengths using a given active material type such as CdSe or PbS. The spectral tuning is easily accomplished in the colloidal quantum dot systems by varying the size of the quantum dots which in turn is tuned by controlling the duration of the chemical reaction used in their synthesis. Thus if one can incorporate the quantum dots into a processable host matrix, then one can realize structures such as waveguides and even more complicated photonic circuits such as the ring resonator as illustrated in figure 2.1a.

![Figure 2.1](image)

Figure. 2.1. (a) Schematic drawing of vertically coupled ring resonator with passive bus waveguides and (b) results of beam-propagation simulation showing greater than 95% coupling efficiency between the lower passive waveguides and the resonator.
Here, the coupling between the waveguides and the microring happens vertically. Results of beam-propagation simulation show efficient coupling between resonator and waveguides as shown in figure 2.1(b). In this geometry the ring itself can be an active structure with quantum dots while the waveguides will be passive structures.

Previously, we were restricted to spin coating colloidal quantum dot based active medium as a thin film followed by a soft bake on an already realized photonic structure. The film’s geometry was a function of the underlying topology of the device. In order to fully realize integration of quantum dots in various structures, the active medium should have viable patterning capabilities. In the following section we will present applications that will motivate why there is a need for pattern capable colloidal quantum dots followed by fabrication techniques and experimental results on the active structures.

2.2 Application and Theory

2.2.1 Amplifier

A waveguide made from an active resist is analogous to optical silica doped with erbium ions that will re-energize the weak signal via stimulated emission without reshaping the signal. At the same time the quantum dot doped waveguides are far smaller in size and hence allows chip-scale integration. In the following figure 2.2, a weak optical signal is successfully coupled into a doped colloidal dot based waveguide of CdSe/ZnS that can conceivably amplify the light once the material is in the gain regime.
2.2.2 Absorption/Saturation Optical Switch

As with transistors in electronics where one can exploit their inversions (i.e. a shift from n-type to p-type or vice versa due to an externally applied voltage) for switching of electrical signals, one can also propose switching applications for the quantum dot based waveguide. Using a fast (fs) pulsed laser, absorption/saturation experiments with quantum dot based waveguides can be performed. For an absorption/saturation experiment, we excite the active medium consisting of PbS quantum dots with a 1550 nm (infrared) femtosecond pulsed laser. At the highest intensity of the pump, the absorbance of the dots is the lowest and hence the weak probe is not absorbed as much and is virtually unaffected corresponding to the ON state of the switch. In the absence of the pump intensity, the weak probe is absorbed and this corresponds to the OFF state (figure 2.3).
Figure 2.3. The expected absorption-saturation dynamics and its use for switching using colloidal quantum dots. The two repeated structures represent the absorption profile of the PbS device during the excitation of two successive femtosecond pump pulses. The crest is where the pump intensity is zero and where absorption of the probe is the highest. The trough is where the absorption is the lowest for the probe where the pump is the highest of intensities.

2.2.3 Ring Resonator Optical Switch

Here, an add/drop and input/throughput configuration was developed geared towards realizing an all-optical switch involving the integration of colloidal quantum dots in the ring geometry. First, the basic principle for the ring resonator will be discussed.

To understand the ring-resonator geometry, we will first discuss coupling between two waveguides as shown in figure 2.4

Figure 2.4. Schematic of the coupled waveguide structure. A probe is coupled to one waveguide and the propagating wave then couples into the other.

Using the dynamics of the fields in the structure as illustrated in figure 2.5, the scattering matrix may be derived.
Figure 2.5. This is a schematic that shows the scattering of fields between the waveguides.

From the arrangement of fields, one may propose the following linear equations.

\[ G = gE_1 + hE_2 ; \quad G = gE_2 + hE_1 \]

\[ F = fE_1 + lE_2 ; \quad F = fE_2 + lE_1 \]

\[ E_{t1} = tE_1 + kE_2 ; \quad E_{t2} = tE_2 + kE_1 \]

Where G and F are fields that couple between the waveguides and g, h, f, and i are the coefficients corresponding to reflection and transmission. \( t \) and \( k \) correspond to the overall transmission and reflection coefficients of the structure. Due to the time reversal symmetry of the Maxwell equations, one can take the conjugation of the fields thereby changing their directions as depicted in figure 2.6.

Figure 2.6. This schematic shows the conjugation of the fields.
The proceeding set of linear equation follow from the preceding schematic.

Conjugation changes direction:

\[ G^* = g^*E_1^* + h^*E_2^* \quad ; \quad G^* = g^*E_2^* + h^*E_1^* \]

\[ F^* = f^*E_1^* + l^*E_2^* \quad ; \quad F^* = f^*E_2^* + l^*E_1^* \]

\[ E_{t1}^* = t^*E_1^* + k^*E_2^* \quad ; \quad E_{t2}^* = t^*E_2^* + k^*E_1^* \]

Time reversal symmetry preserves physics i.e.:

\[ E_1^* = t^*E_{t1}^* + k^*E_{t2}^* \quad ; \quad E_2^* = t^*E_{t2}^* + k^*E_{t1}^* \]

From these equations we get:

\[ \begin{pmatrix} E_1^* \\ E_2^* \end{pmatrix} = \begin{pmatrix} t & k \\ \bar{k} & \bar{t} \end{pmatrix} \begin{pmatrix} E_{t1}^* \\ E_{t2}^* \end{pmatrix} \]

But from the conjugation:

\[ \begin{pmatrix} E_{t1}^* \\ E_{t2}^* \end{pmatrix} = \begin{pmatrix} t^* & k^* \\ \bar{k}^* & \bar{t}^* \end{pmatrix} \begin{pmatrix} E_1^* \\ E_2^* \end{pmatrix} \]

Taking the inverse one must have that:

\[ \begin{pmatrix} E_{t1}^* \\ E_{t2}^* \end{pmatrix} = \frac{1}{(tt-kk)} \begin{pmatrix} \bar{t} & -k \\ -k & t \end{pmatrix} \begin{pmatrix} E_1^* \\ E_2^* \end{pmatrix} \]

\[ n |E_1|^2 - n |E_{t1}|^2 = -n_t |E_2|^2 + n_{\bar{t}} |E_{t2}|^2 \]

for waveguides of same material \( n = n_t \Rightarrow |E_1|^2 + |E_2|^2 = |E_{t1}|^2 + |E_{t2}|^2 \)

\[ = |t|^2|E_1|^2 + |ar{k}|^2|E_1|^2 + |\bar{t}|^2|E_2|^2 + |k|^2|E_2|^2 + t^*k^*E_1^*E_2 + k^*t^*E_2^*E_1 + \bar{t}^* \bar{k}^*E_2^*E_1 + \bar{k}^* \bar{t}^*E_1^*E_2 = 0, \]

\[ k^*t + \bar{t}^* \bar{k} = t^*k + \bar{k}^* \bar{t} = 0 \]

\[ |t|^2 + |ar{k}|^2 = |\bar{t}|^2 + |k|^2 = 1 \]

\[ \frac{-k}{(tt-kk)} = k^* \quad , \quad \frac{-\bar{k}}{(tt-\bar{kk})} = \bar{k}^* \]
For convenience one may choose \( \delta = 2\pi \mathbf{m} \) and therefore \( \mathbf{k} \) will be purely imaginary.

Now the ring structure will be introduced as depicted in figure 2.7.

\[
\frac{t}{(tt-\mathbf{k})} = t^*, \quad \frac{\bar{t}}{(tt-\mathbf{k})} = \bar{t}^*, \quad \Rightarrow \quad \frac{t^*}{|tt-\mathbf{k}|} = t \Rightarrow \quad \frac{t}{(tt-\mathbf{k})} = \frac{\bar{t} - \mathbf{k}}{1} = 1
\]

\[
\therefore \quad \bar{t} e^{i\delta} = t^*, \quad -\mathbf{k} e^{i\delta} = \mathbf{k}^*, \quad \Rightarrow
\]

\[
\begin{pmatrix}
E_{t1} \\
E_{t2}
\end{pmatrix} = 
\begin{pmatrix}
t & k \\
\bar{k} & \bar{t}
\end{pmatrix} 
\begin{pmatrix}
E_1 \\
E_2
\end{pmatrix} = 
\begin{pmatrix}
t & k \\
\bar{k} & t^* e^{-i\delta}
\end{pmatrix} 
\begin{pmatrix}
E_1 \\
E_2
\end{pmatrix}
\]

(2.1)

Using matrix (2.1), the transmitted field in the waveguide is now

\[
E_{t2} = E_2 e^{i\theta}; \quad E_2 = \frac{kE_1}{e^{i\theta} - t^* e^{-i\theta}}; \quad E_{t1} = \frac{te^{i\theta} - |t|^2 + k^2}{e^{i\theta} - t^*} E_1
\]

\[
= \frac{te^{i\theta} - |t|^2 - |k|^2}{e^{i\theta} - t^*} E_1 = \frac{te^{i\theta} - 1}{e^{i\theta} - t^*} E_1
\]

\[
P_{out} \propto \left| \frac{E_{t1}}{E_1} \right|^2 = \frac{1 + |t|^2 - 2|t| \cos(\theta + \beta)}{1 + |t|^2 - 2|t| \cos(\theta + \beta)} = I \text{ where } \beta \text{ is the phase of } t \text{ and } \theta \text{ is the phase acquired from propagation in the ring.}
\]
Regardless of power input and ignoring loss in the ring, power is conserved. Next, an investigation of the other waveguide that is coupled to the waveguide is depicted in figure 2.8.

![Figure 2.8. Ring coupled to add/drop waveguide.](image)

Similar matrix for add/drop waveguide gives

\[
\begin{pmatrix}
E_{t3} \\
E_2
\end{pmatrix} =
\begin{pmatrix}
t_2 & k_2 \\
k_2 & t_2^*
\end{pmatrix}
\begin{pmatrix}
E_3 \\
E_{t2}
\end{pmatrix}
\]

For the full add/drop and input/throughput configuration, the operations become

\[
\begin{pmatrix}
E_{t3} \\
E_2
\end{pmatrix} =
\begin{pmatrix}
t_2 & k_2 \\
k_2 & t_2^*
\end{pmatrix}
\begin{pmatrix}
E_3 \\
E_{t2}e^{i\theta_2}
\end{pmatrix}
\]

\[
\begin{pmatrix}
E_{t1} \\
E_{t2}
\end{pmatrix} =
\begin{pmatrix}
t & k \\
k & t^*
\end{pmatrix}
\begin{pmatrix}
E_1 \\
E_{t2}e^{i\theta_2}
\end{pmatrix}
\]

However, for the switching application, light is launched into the entrance of the input waveguide only. The out power of interest will be measured from the throughput port.

Therefore \( E_3 = 0 \). The result is
Using the lithography techniques and protocols discussed in the Appendix B, the colloidal quantum dots can be integrated into the ring structure such as in figure 2.9.

\[ E_{t1} = t E_1 + k E_2 e^{i\theta}; \quad E_2 = t_2^* E_2 e^{i\theta}; \quad E_{t2} = k^* E_1 + t^* E_2 e^{i\theta} \]

\[ \Rightarrow E_{t1} = t E_1 + \frac{k^2 t_2^* e^{i\theta}}{1 - t^* t_2^* e^{i\theta}} E_1 = \frac{t - |t|^2 t^2_2 e^{i\theta} - |k|^2 t_2^* e^{i\theta}}{1 - t^* t_2^* e^{i\theta}} E_1 = \frac{t - t_2^* e^{i\theta}}{1 - t^* t_2^* e^{i\theta}} E_1 \]

\[ P_{out} \propto \left| \frac{E_{t1}}{E_1} \right|^2 = \frac{|t|^2 + |t_2|^2 - 2 |t||t_2| \cos \theta + \beta}{1 + |t|^2 |t_2|^2 - 2 |t||t_2| \cos \theta + \beta} \]

For \( t \) and \( t_2 \) are real and equal \( P_{out} \propto \frac{2t^2(1 - \cos \theta)}{1 + t^4 - 2|t|^2 \cos \theta} \) (2.2)

\[ \theta = \frac{2\pi n_{\text{ring}}}{\lambda_{\text{ring}}} = \frac{2\pi n_{\text{ring}} n_{\text{eff}}}{\lambda} \]

Using the lithography techniques and protocols discussed in the Appendix B, the colloidal quantum dots can be integrated into the ring structure such as in figure 2.9.

Figure 2.9. SEM image of the add/drop and input/throughput made entirely of quantum dots. Due to the “active resist”, one has the ability to construct various geometries such as this. The goal is to have a concentration of dots that would show gain dynamics in the ring resonator.

The optical nonlinearity of the dots will be used to tune the phase acquired in the ring [23]:

\[ \theta = \frac{2\pi n_{\text{ring}} n_{\text{eff}}}{\lambda} + n_{\text{dots}} I_{\text{ring}} \frac{2\pi n_{\text{ring}}}{\lambda} \] (2.3)
$n_{dots}$ is the nonlinear contribution of the dots due to their 3\textsuperscript{rd} order electric susceptibility. $I_{ring}$ is the intensity in the ring. The microring resonator is pumped with a high intensity beam. The operation of the ring resonator based switch is as follows: The microring switch is designed so that the pump corresponds to one of the modes of the ring and the probe is slightly spectrally shifted from a second resonance. The optical nonlinearity of the quantum dots spans a broad spectral range that covers both the pump and probe wavelengths. In the presence of the pump signal, the nonlinear refractive index introduces a shift in the resonance of the active ring. This in turn results in the probe signal which was previously in the ON (transmissive) state to go to the OFF state (reflective). This is shown schematically in Fig. 2.10.

Figure 2.10. Simulation of microring switch. Pump must correspond to the mode of the ring resonator where transmission remains the same during off and on states of the probe.
2.3 Fabrication and Experimental Results

We dope 10ppm of CdSe/ZnS dots in SU8, a negative photo resist, provided by MicroChem Inc. The recipe used is: 0.5 mL of CdSe/ZnS colloidal quantum dots is dispersed in 1mL of PMMA. This mixture is then dispersed in 10 mL of SU8 with a viscosity of 45cSt. This gives a concentration of about 0.435 ppm of CdSe in SU8. The solution is then placed in a sonicator for 2hrs between 40°C and 48°C. The result is an active resist. However the new environment of the quantum dots does change certain properties of the quantum dots. As shown previously by us [24], the photoluminescence of the colloidal quantum dots is a function of the environment they are suspended in as depicted in Fig. 2.11.

Figure 2.11. Semiconductor cluster of CdSe/ZnS dots exhibit decrease in steady state luminescence intensity and reduction in lifetime when introduced into different solvent environments. [Taken from Vinod M. Menon Saima Husaini Nicky Okoye Nikesh V. Valappil Integrated Photonics Using Colloidal Quantum Dots. Journal of Nanophotonics, 3(1): 031608, November 2009.]
The lifetime of the colloidal quantum dots in SU-8 suggests faster decay rates. However, the faster decay is also accompanied by reduction in the emission intensity. This indicates an increase in non-radiative decay processes. While this might be detrimental to the development of devices that require high luminescence yields, for applications such as switching, the faster recovery times may actually prove to be beneficial for developing high repetition rate ultrafast switches.

Now that we developed an active resist solution, we fabricated planar photonic structures using electron beam lithography. The details of electron beam lithography are discussed in appendix B. We were able to pattern resist geometries doped with colloidal quantum dots with PMMA and SU-8. They all showcased the lithographic consistencies of the active resists. In particular, we were able to achieve the same critical features with the doped resists as with the un-doped resist as illustrated in figures 2.12 and 2.13. Furthermore, the dosages for the resists as well as other protocols remained the same.

![Figure 2.12](image1.png)

Figure 2.12. Figure on the left is an SEM image of two coupled PMMA disks embedded with colloidal quantum dots fabricated using electron beam lithography. The image on the right shows the 959 nm gap between the disc resonators.
Figure 2.1. SEM of two coupled SU8 disks “doped” with colloidal dots fabricated using electron beam lithography. The figure on right shows that critical features of less than 400nm can be obtained.

We then successfully patterned active waveguide devices integrated into passive waveguide devices (figures 2.14 and 2.15).

Figure 2.14. These are SEM images showing achieved cross sections of waveguide. The right image shows the “launch port” of the passive guide. The left image shows the section joining the active to the passive component of waveguide.
Figure 2.15. (a) Optical microscope image of active waveguide (with dots) integrated with passive waveguide. (b) Luminescence observed from the integrated device under optical excitation indicating emission from only the active guide and no clustered emission from elsewhere. The ovals that flank the waveguide on both sides are alignment marks.

The active waveguides were pumped from the top and the luminescence from the quantum dots were found to propagate along the waveguide structure. The optical excitation was done using an Argon ion laser (488 nm) (figure 2.16).

Figure 2.16. An argon laser is diverted from its source to another workbench where a mirror reflects the light into a fiber coupler. The argon light is then propagated along a fiber that is coupled into the fabricated polymer wave guide that rests on an xyz stage. The light emerging from the exit port of the waveguide is coupled to an objective with xyz control that is connected to a detector connected to a computer.

The emission from the radiation leaking from the waveguide as the light propagates was observed using a long pass filter attached CCD camera. The notable aspects of the
demonstration include the fact that quantum dots were located precisely in the region of the active waveguide as illustrated by the fact that we don’t see any emission from other regions. In addition, there is very little scattering observed indicating smooth waveguide edges which is also established from the SEM images shown previously.

To demonstrate the amplification property of the active waveguide, we need to push the quantum dots into the gain regime. In colloidal quantum dots, the first signature of gain is usually the appearance of amplified spontaneous emission as shown in Fig. 2.17.

Figure 2.17 As pump intensity increases photoluminescence of CdSe increases a) CdSe capped with ligands b) CdSe core with ZnS shell capped with ligands (Insets) Superlinear pump intensity dependence of the stimulated emission (circles) showing threshold. Sublinear dependence of the emission is outside the sharp stimulated emission peak (squares). [Taken from Klimov V. I., Mikhailovsky A. A., Xu S., Malko A., Hollingsworth J. A., Leatherdale C. A., Eisler H. J., Bawendi M. G., Science Magazine (2000) vol. 290 (5490) pp314-317]
If the dots are excited with enough pump intensity, population inversion can occur [25,26]. Once population inversion is achieved then the emission spectrum of the dots should get narrower due to stimulated emission.

In the case of CdSe quantum dots, Klimov et. al. demonstrated amplified spontaneous emission, (ASE), around 2eV. When the dots are capped with ZnS shell, ASE is observed at the peak photoluminescence.

Our experiments were carried out in the continuous wave pump regime and hence did not provide sufficient pump energy to obtain gain. We did observe emission and transmission through a 90 degree bent active waveguide with minimal scattering as shown in Fig. 2.18. However using a pulsed NdYAG laser to observe gain in the same system resulted in the degradation of the active waveguides most likely due to structural changes introduced by the heat to the polymer host.

![Image](image_url)

Figure 2.18. The image a) shows the luminescence and propagation of said luminescence of a 90 degree bent active waveguide after a focused excitation at the bend with an argon laser. The graph b) shows the spontaneous emission response of the 90 degree bent waveguide after excitation with an Argon ion laser at different pump intensities. At higher intensities, the bandwidth increase implies that we have not reached the gain threshold. We require more than 50mw to achieve population inversion.
It should however be noted that other work from our group showed ASE from the same quantum dots which were embedded in an all dielectric microcavity structure [27] indicating the role of the host matrix on the ASE. Thus, to circumvent the destruction of the structure that is designed and fabricated, another approach that takes advantage of the pattern capabilities of an active resist needs be explored.

**2.4 Future Approach**

As a solution to the above discussed issue, we propose using an amorphous solid waveguide with a slot filled with an active medium such as the slot waveguide in figure 2.19.

![Figure 2.19](image)

Figure 2.19. This is a schematic illustrating a bent waveguide incorporating the integration of an active thin film. The active material is sandwiched between two dielectric materials. The dielectrics could represent solids and/or amorphous solids.

The dielectric slab might be a higher index material than the nonlinear material such as the quantum dots. In figure 2.20, a slot waveguide device schematic with the “cladding” for the nonlinear material is shown with a simulation showing mode confinement in the “core” of the waveguide.
Figure 2.20. (a) Figure on the left is a schematic of an optical material between two dielectric SiNₓ slabs fabricated on top of a deposited SiO₂ film grown on Si. The arrow shows direction of propagation of light and the concentric rings on the entrance port of the waveguide structure is the Gaussian spot size of a laser that is coupled into the device at near field. (b) optical confinement of coupled light into the slot waveguide mode due to sub-wavelength dimension of nonlinear optical slot thickness.

The confinement is due to the boundary conditions that arise in Maxwell’s equation for the transverse magnetic TM mode. The operational principle is the discontinuity of the normal component of the E field at the interface between the low and high index media [28]. The role of the electric displacement of the macroscopic field may be expressed according to the following integral.

\[ \int D \cdot da = \rho_{\text{excess}} \]

Where \( D \) is the electric displacement integrated over a Gaussian “pillbox” that encapsulates a small constituent of the interface between the index core material and the higher index slab. Since all charge densities are bounded, ones sets the excess charge density, \( \rho_{\text{excess}} \), to zero giving a continuity for the electric displacement perpendicular to the interface of the SiNₓ and nonlinear optical material. This results in a discontinuity in the normal electric field due to the difference in the electric permittivities.

\[ E_{\text{NOM}} \epsilon_{\text{NOM}} = E_{\text{SiN}_x} \epsilon_{\text{SiN}_x} \quad \text{and} \quad \epsilon_{\text{NOM}} < \epsilon_{\text{SiN}_x} \Rightarrow E_{\text{NOM}} > E_{\text{SiN}_x} \]

Where NOM stands for nonlinear optical material

For waveguide modes, the EM field will propagate in the higher index material and attenuate exponentially into the lower index material of the NOM due to total internal
reflection. However, for the TE modes normal to the SiNx/NOM interface, the electric field to the immediate top of the interface in the SiNx region will be less than the electric field in the immediate bottom of the interface in the NOM region. The same situation occurs for the NOM/SiNx interface in the figure 2.20a. The attenuation of the fields is described according to the following.

\[
\begin{align*}
\text{NOM region is in the space} & \quad \frac{t}{2} \leq y \leq \frac{t}{2} \\
E(y)_{\text{NOM}} & \sim e^{-y + \frac{t}{2} y} \quad \text{for} \quad \frac{t}{2} \leq 0 \\
E(y)_{\text{NOM}} & \sim e^{y - \frac{t}{2} y} \quad \text{for} \quad 0 \leq \frac{t}{2}
\end{align*}
\]

When \(ty \ll 1\), the field \(E(y)_{\text{NOM}}\) remains high throughout the NOM slot material. Therefore, for sub-wavelength optical confinement, one must have thin slots such that the thickness is less than the decay length \(\frac{1}{y}\). In figures 2.21 to 2.24 an array of horizontal slot waveguide [29] geometries embedded with a NOM fabricated using E beam lithography is shown.

Figure 2.21. Waveguide arrays made of SiNx, NOM, SiNx slot on SiO\(_2\) grown on GaAs
Figure 2.22. Magnified waveguide. Magnification shows presents of micro grass.

Figure 2.23. Waveguide profile with cross section after GaAs was cleaved

Figure 2.24. This is an SEM image showing achieved cross sections of waveguide.
These slot waveguides were fabricated with a nonlinear proprietary material (Lightwave Technology) as the slot core. First SiO$_2$ is deposited using PECVD at base pressure 400mT with silane and N$_2$O at sccm of 52 and 180, respectively. Then SiNx is grown with base pressure of 800mT with nitrous oxide, ammonia, and nitrogen with flowrates of 180 sccm, 20 sccm, and 88sccm respectively. The NOM is spin coated. Positive resist using $\frac{1}{2}$ micron PMMA was used as mask etch. Reactive ion dry etching was then done at 40 sccm of CF$_4$ and 10 sccm of O$_2$ at 100 watts of RF power. Slot waveguides of about 1 micron were produced. However, there was a substantial amount of micro grass (figure 2.22) surrounding waveguide structures due to interrupted periods of etching. It was required to etch in steps so that the etch mask still existed while etching through nitride to achieve the one micron slot devices. In addition when colloidal quantum dots where sandwiched between the two SiNx slabs as in the case of the proprietary NOM, etching through the dot matrix was not a reproducible occurrence as illustrated in figure 2.25.

![SEM image illustrating how the quantum dot matrix itself acts as an etch mask. Etching does not penetrate matrix. Instead, top dielectric slab is etched inward and from the top.](image-url)
However, incorporating the quantum dots into PMMA is expected to alleviate this issue since we have already demonstrated the successful lithography of quantum dot embedded PMMA structures. Using the alignment protocols discussed in appendix B, we can align an active PMMA slot geometry to the bottom and top dielectric waveguides of slightly larger pitches. This ensures that the etching process won’t involve etching of the colloidal quantum dot medium.

**Summary**

With the quantum dot doped resist, various geometries with nonlinear properties of semiconductor nanomaterials can be practically fabricated without any new protocols in chip fabrication. The novelty is the active resist itself. Here we showed two geometries that have the potential to be used in an all optical- signal processing integrated circuit. These were the waveguide amplifier and the waveguide saturation/absorption switch, and the microring optical switch.
Chapter 3

Colloidal Quantum Dot Based Microcavity LED

3.1 Motivation

Changing the environment of colloidal quantum dots leads to a modification in photoluminescence of the dots [30-33]. Microcavities have been used for enhancing spontaneous emission rates due to the increase in photon density of states at the resonant wavelength [34-38]. Traditionally, complicated growth techniques such as MBE and Metal Organic Chemical Vapor Deposition (MOCVD) are the most widely used techniques to fabricate microcavity structures [37, 39, and 40]. A simpler approach is to use amorphous dielectric materials as the mirrors and the semiconductor as the active material in the cavity layer. In this context, colloidal quantum dots are very attractive since they can be deposited via simple techniques such as spin or dip coating. The earliest reports on the incorporation of colloidal quantum dots in microcavities involved Whispering-Gallery-Mode (WGM) structures. Here, colloidal quantum dots were used with microsphere and microring geometries [36, 41, and 42]. One dimensional microcavity systems embedded with CdSe quantum dots have also been realized in the past [43-48]. Although there have been reports using all-dielectric microcavity structures for mode confinement [46], there have not been any reports of enhancement of gain using such systems. Here we report enhancement of photoluminescence from colloidal quantum dots in a one dimensional photonic crystal where each mirror is built by a periodic variation of refraction indices referred to as a Distributed Bragg Reflector (DBR). Figure 3.1 illustrates the basic configuration of the PbS microcavity DBR.
3.2 Theory

We fabricate our one dimensional microcavity using the Fabry-Perot etalon configuration as depicted in figure 3.2.

Figure 3.2. Illustration of multiple wave interference from a cavity.

It is an interferometer composed of a cavity of thickness $d$ and index of refraction $n$ in between two mirrors. The cavity is the layer where electromagnetic radiation emitted from the material scatters at the mirror interfaces. The resultant interference pattern is due to the superposition of transmitted waves that scatter from the mirror surfaces. The
adjacent scattered waves at a given mirror surface are related by an optical path length that leads to a phase shift $\delta$ [49]. $\delta$ may be expressed as follows.

$$\frac{4\pi nd \cos \theta}{\lambda}$$ [49] \hspace{1cm} (3.1)

Where $\lambda$ is the wavelength of the scattered light in free space and the meaning of $\theta$ is depicted in figure 3.2. By adding all the transmitted waves, the transmission coefficient becomes

$$\frac{1}{1 + \left( F \sin \frac{\theta}{2} \right)^2}$$ [49].

And the reflection coefficient may be derived from the transmission by noting that transmission + reflection = 1 if we ignore absorption.

$$\frac{\left( F \sin \frac{\theta}{2} \right)^2}{1 + \left( F \sin \frac{\theta}{2} \right)^2}$$ [49]

Where $F = \frac{2r}{1-r}$ and $r$ is the reflection amplitude at the mirrors. Both the transmissions and reflections are simulated in figures 3.3 and 3.4 for different reflection amplitudes.

Figure 3.3. Matlab simulation of Fabry-Perot etalon for different reflection amplitudes $r$. Phase corresponds to $\delta$. Reflections are minimum when $\delta = 2m\pi$ where $m$ is an integer.
Figure 3.4. Matlab simulations of Fabry-Perot etalon for different reflection amplitudes r. Phase corresponds to $\delta$. Transmissions are maximum when $\delta = 2m\pi$ where m is an integer.

In our Fabry-Perot etalon, the cavity houses PbS colloidal quantum dots in toluene. These quantum dots are the source of electromagnetic radiation that is scattered within the cavity and at the mirror interfaces. The electromagnetic radiation is due to the photoluminescence of the colloidal dots as illustrated in figure 3.5. In figure 3.3, there is a periodic domain of wavelengths where the reflections are maximum. These domains are stopbands where there is no propagation of the photoluminescence. However, photoluminescence is enhanced where the dips are present. Figure 3.6 is an overlay of a Fabry-Perot etalon made with DBR mirrors over the photoluminescence of the PbS in toluene. We choose the DBR mirror format over metal mirrors due to the absorption issues of metal. The microcavity structure design consists of DBRs made of alternating layers of SiO$_2$ and SiNx that are quarter wavelength thick. The quantum dots are located in the cavity layer and are designed to be half wavelength thick. The simulation shown below does not take into account the absorption of the quantum dots and hence the experimentally observed cavity linewidth is larger than what is theoretically predicted. In
addition to enhancement in the spontaneous emission rate, emission from the cavity is
directional.

Figure 3.5. Photoluminescence of PbS colloidal quantum dots in toluene when excited
with 488 nm continuous wave laser.

Figure 3.6. Simulated reflectivity of microcavity DBR (blue) superimposed on
photoluminescence of PbS quantum dots in toluene (black).

3.3 Fabrication and Experimental Results

Plasma enhanced chemical vapor deposition (PECVD) is used to fabricate the one
dimensional photonic crystal. Gases of N₂O and Si₃H₄ at a base pressure of 400 mT flow
into the system at 180sccm and 52sccm respectively where they are turned into plasma by an RF-signal applied between the top and bottom electrodes of the chamber. The free radicals created bombard a silicon substrate and deposit a film of SiO$_2$. A gas mixture of N$_2$, NH$_3$ and Si$_3$H$_4$ at a base pressure of 800 mT flow into the system at 180 sccm, 20 sccm, and 88 sccm respectively. The result is a thin film of SiNx.

Alternate layers of SiO$_2$ and silicon poor silicon nitride (SiNx) are deposited on a silicon wafer at a temperature of 150 °C. The SiNx has an index of refraction of 1.77 and a thickness of 219 nm. The SiO$_2$ layer has an index of 1.45 and a thickness of 267 nm. The layers are designed to be a quarter wavelength thick (λ/4n). Here, λ is the wavelength that the microcavity selects for transmission and the n is the index of refraction of the layer. The alternate layer repeats 11 times with an added 219 nm silicon nitride deposition giving a 11.5 period DBR mirror. On top of the DBR structure, 267 nm of SiO$_2$ is deposited followed by deposition of $10^{-3}$ mg of PbS in a 1 mL solution of toluene via spin coating. The bottom DBR with the PbS layer on top is then placed on a hotplate at 150 °C for 5 minutes to remove the solvent resulting in a PbS film of 60 nm thickness. An additional 300 nm of silicon dioxide is deposited on top of the PbS layer. Another DBR mirror is then deposited once again at 150 centigrade on the device. The low temperature growth is critical to the integrity of the quantum dots. The top DBR mirror is an 8 periodic structure with an additional 219 nm layer of silicon nitride deposited on top. The result is a microcavity with PbS quantum dots between 8.5 and 11.5 period DBR mirrors. A second device was created similarly but with a 16.5 and 14.5 bottom and top DBR, respectively.
To characterize the modification in spontaneous emission from the microcavity, the devices are excited by continuous wave Argon laser as shown in figure 3.7. The laser wavelength does not correspond to a standing mode of the structure. It freely propagates through the device when it is incident on the top DBR mirror. It transmits and excites the PbS quantum dots. Photoluminescence emission from dots is collected perpendicularly from the surface of the top DBR mirror. The photoluminescence emission for the second device is also collected from angles 0° to 30° from the surface of the device. This is to determine photoluminescence spatial distribution at 1554 nm.

Figure 3.7. Experimental setup involves excitation with 488 nm at an angle while collection is done perpendicular to surface of top DBR

Figure 3.8 shows the differences of photoluminescence enhancement for the first and second devices. The microcavity devices show enhancement in emission over a narrow spectral range while suppressing the emission at other wavelengths. This is due to the increase in photon density of states at the resonant wavelength. This enhancement in spontaneous emission due to modification of the photon density by altering the environment surrounding the emitter is referred to as the Purcell effect [33]. The density
of states in the cavity is greater than the density of states in vacuum leading to enhancement of the given wavelength. The enhancement is directly proportional to the quality factor of the environment of the emitters. The Purcell effect is greater in the second device with a cavity line width of approximately 9.3 nm giving a quality factor ($Q$ factor), $\lambda/\Delta\lambda$, of ~168 at 1554 nm. The first device gives a line width of approximately 22 nm had a $Q$ factor of ~ 71.

![Graph](image1.png)

**Figure 3.8.** a) Measured photoluminescence at 22mW for the microcavity structure with 11.5 and 8.5 bottom and top DBRs, respectively. b) Measured photoluminescence at 1mW for the structure with 16.5 and 14.5 bottom and top DBRs, respectively.

It is apparent that the increase in the number of pairs of DBR mirrors gives a device with a better finesse. From the following equation, $\frac{\lambda^2}{2n\Delta\lambda}$ [50], we find that the finesse of
the first device is 60 and the second is 142. We now show the actual reflectivity of the created devices to confirm origin of enhancement. Reflectivity is measured by incidence of a white light source perpendicular to the surface of the top DBR of the microcavity devices. Collection of reflectivity is also done perpendicularly. The line widths of the two devices nearly match the dip locations of the measured reflectivities of the two microcavities. The photoluminescence profiles are compared to the reflectivities of both vertical cavity resonators in figure 3.9.

Figure 3.9. Reflectivity and photoluminescence. The solid squares correspond to the reflectivity while the solid line corresponds to the photoluminescence. Enhancement at wavelength of 1550 nm for the microcavity with (a) 11.5 and 8.5 bottom and top DBRs respectively and (b) 16.5 and 14.5 bottom and top DBRs, respectively.
PbS dots embedded within the SiO$_2$ cavity layers without the top and bottom DBR mirrors show photoluminescence without enhancement. The peak photoluminescence is blue shifted from the PbS quantum dots without the dielectric geometry (figure 3.10). The SiO$_2$ dielectric slab is found to reduce the photoluminescence when compared to the original photoluminescence measurements of the bare quantum PbS dots in figure 3.5. It is the incorporation of the mirrors that condense the original 250 nm line width to <10 nm and enhance the ~1550 nm wavelength as illustrated in figure 3.11.

Figure 3.10. Photoluminescence of PbS quantum dots “sandwiched” within the SiO$_2$ layers without the DBR mirrors (black) is superimposed on bare quantum dot emission (red). Dielectric slab reduces emission by a factor of 1000 and shifts peak photoluminescence to shorter wavelengths. Dielectric construct requires mirrors for enhancement of wavelength peak.
Figure 3.1. The black spectra corresponds to the photoluminescence from the control sample and the blue spectrum of the dots integrated into the 16.5/14.5 top/bottom DBR based microcavity. This illustrates the narrowing of line width of the original photoluminescence by a factor of ~27 and photoluminescence enhancement at ~1550 nm.

Angle dependent photoluminescence measurements were done on the 16.5/14.5 top/bottom DBR based microcavity to characterize the directionality in emission that is due to the microcavity structure (figure 3.12). Measurements are taken up to 30 degrees at 5 degree intervals from the axis of the microcavity structure. Reduction of photoluminescence at 1554 nm at increasing angles of collection demonstrates the directionality of the microcavity device as predicted by equation 3.1. From equation 3.1 we set $\theta = 0$ and set the phase $\delta = 2\pi$. These constraints lead to a thickness of $\lambda/2n_{cavity}$ for the cavity. This is required for normal directionality of the beam. However, the growth process to fabricate DBR mirrors applicable to the short wavelength infrared requires long deposition times. In utilizing our PECVD, growth rates of the dielectric layers change during the long process. The DBR mirrors generally consist of dielectric films that either decrease or increase from the original $\lambda/4n_{dielectric}$ thickness. We made
various microcavities with thicknesses ranging from -20% to 20% from the derived \( \lambda/2n_{cavity} \). The actual thickness that gives us the \( \sim 1550 \) nm emission with directionality is \( \sim 17\% \) greater than \( \lambda/2n_{cavity} \).

![Diagram](image.png)

Figure 3.12. Measured angular emission from device 2 at angles ranging from 0 to 30 degrees with respect to the cavity axis.

Power dependent measurements were carried out using the Argon ion laser as the pump source. The steady state spectra are shown in figure 3.13 and the \( P_{out} \) versus \( P_{in} \) results are shown in figure 3.14. Linear increase in the output power is seen but there is no reduction in linewidth. In addition, no threshold behavior is observed. All of these observations indicate that we did not observe the system transitioning into the gain regime and we did not observe the appearance of ASE. As noted above, these measurements were carried out in the CW regime and hence the pump energy was low. We anticipate the use of pulsed excitation to overcome this issue and observe ASE from these microcavity structures.
Figure 3.13. a) Measured photoluminescence with increasing pump power collected perpendicularly from device 2. Pump power ranges from 50 to 1 mW. Line width does not broaden at lower intensities. Pump intensities as low as 1 mW maintain spectral line width.

Figure 3.14. Power dependent plot showing almost linear increase in the output power indicating that we have not reached the gain regime of the quantum dot microcavity.
Summary

In summary, we have successfully demonstrated the incorporation of 1550 nm emitting PbS quantum dots into a microcavity structure without destroying quantum dots during high temperature growth using PECVD. The photoluminescence enhancement due to the Purcell effect was observed at 1550 nm due to the enhancement of the photon density of states provided by the microcavity. Reduction in linewidth by a factor of 27 and an enhancement in the peak intensity by ~1.66 was observed. The Q factor of the cavity was 168. The power dependent characteristics did not show any threshold behavior indicating that the PbS quantum dots embedded microcavity were still below the gain regime. The present demonstration can easily be extended to other spectral regions by designing appropriate DBRs and choice of quantum dots. The demonstration of a 1550 nm vertical cavity emitter that is compatible with silicon substrate is highly attractive for realizing low-cost silicon compatible electronic-photonic integrated chips. In the future it will be necessary to develop appropriate electrical injection schemes to make the device monolithically integrated. However the present demonstration is an encouraging first step in the direction for developing 1550 nm emitting silicon compatible lasers.
Appendix A

A.1 Variational Method

How does one study the arrangement of a large number of atoms? In using the molecular orbital theory [51] we use the variational approach [1,52]. We may use a Linear Combination of Atomic Orbitals (LCAO) as a trial function to approximate the energy to the ground state of the Hamiltonian. We start with the following LCAO:

\[ |\Psi\rangle = \sum_\alpha c_\alpha |\psi_\alpha\rangle \]

Normalized: \[\frac{\sum_\alpha c_\alpha |\psi_\alpha\rangle}{\langle \psi | \psi \rangle}\]

The coefficients, \( c_\alpha \), are expansion coefficients and the \( |\psi_\alpha\rangle \) are the atomic orbitals at atomic sites designated by the subscript \( \alpha \). In deriving the energy for the trial state, the Hamiltonian is written:

\[ \langle \psi | H | \psi \rangle \equiv E \langle \psi | \psi \rangle \]

\[ \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = E \]

Keep in mind that the trial function is generally not an eigenfunction of the system. Furthermore, there is no assumption of normalization and \( E \) is not an eigenvalue. Here, we are not attempting to solve the Schrödinger equation. We are attempting to approximate the ground state energy by minimizing the energy functional \( E \). This is done by differentiating the energy functional with respect to the trial vectors \( |\Psi\rangle \) and \( \langle \Psi| \).

\[ \delta \left[ \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \right] = E \]

\[ \delta \langle \psi | H | \psi \rangle = \langle \delta \psi | H | \psi \rangle + \langle \psi | H | \delta \psi \rangle \]
\[ \delta \langle \Psi | \Psi \rangle = \langle \delta \Psi | \Psi \rangle + \langle \Psi | \delta \Psi \rangle \]

\[ \Rightarrow \delta E = \frac{\langle \delta \Psi | H | \Psi \rangle + \langle \Psi | H | \delta \Psi \rangle}{\langle \Psi | \Psi \rangle} - \frac{\langle \Psi | H | \Psi \rangle (\langle \delta \Psi | \Psi \rangle + \langle \Psi | \delta \Psi \rangle)}{\langle \Psi | \Psi \rangle^2} \]

In order to minimize the energy functional, the variation of the functional is set to 0.

\[ \delta E = 0; \quad \frac{\langle \delta \Psi | H | \Psi \rangle + \langle \Psi | H | \delta \Psi \rangle}{\langle \Psi | \Psi \rangle} - \frac{\langle \Psi | H | \Psi \rangle (\langle \delta \Psi | \Psi \rangle + \langle \Psi | \delta \Psi \rangle)}{\langle \Psi | \Psi \rangle^2} = 0 \]

\[ \langle \Psi | \Psi \rangle (\langle \delta \Psi | H | \Psi \rangle + \langle \Psi | H | \delta \Psi \rangle) - \langle \Psi | H | \Psi \rangle (\langle \delta \Psi | \Psi \rangle + \langle \Psi | \delta \Psi \rangle) = 0 \]

For real \( \langle \Psi | \Psi \rangle \) there is a factor of 2 that may be cancelled out.

\[ \Rightarrow \langle \Psi | \Psi \rangle \langle \delta \Psi | H | \Psi \rangle - \langle \Psi | H | \Psi \rangle \langle \delta \Psi | \Psi \rangle = 0 \]

As an ansatz, the change in either vector is due to the coefficient parameters changing.

\[ \langle \delta \Psi \rangle = \sum_\alpha \delta C_\alpha \langle \psi_\alpha \rangle \]

The rest follows via substitution and algebra:

\[ \langle \Psi | \Psi \rangle = \sum_\beta \sum_\alpha C_\beta C_\alpha \langle \psi_\beta | \psi_\alpha \rangle \]

\[ \langle \delta \Psi | \Psi \rangle = \sum_\beta \sum_\alpha \delta C_\beta C_\alpha \langle \psi_\beta | \psi_\alpha \rangle \]

\[ \langle \Psi | H | \Psi \rangle = \sum_\beta \sum_\alpha C_\beta C_\alpha \langle \psi_\beta | H | \psi_\alpha \rangle \]

\[ \langle \delta \Psi | H | \Psi \rangle = \sum_\beta \sum_\alpha \delta C_\beta C_\alpha \langle \psi_\beta | H | \psi_\alpha \rangle \]

\[ \langle \Psi | \Psi \rangle \langle \delta \Psi | H | \Psi \rangle - \langle \Psi | H | \Psi \rangle \langle \delta \Psi | \Psi \rangle = \]

\[ \sum_\beta \sum_\alpha C_\beta C_\alpha \langle \psi_\beta | \psi_\alpha \rangle * \sum_\mu \sum_\nu \delta C_\mu C_\nu \langle \psi_\mu | H | \psi_\nu \rangle - \sum_\rho \sum_\sigma C_\rho C_\sigma \langle \psi_\rho | H | \psi_\sigma \rangle * \sum_\xi \sum_\zeta \delta C_\xi C_\zeta \langle \psi_\xi | \psi_\zeta \rangle = 0 \]

And from \( \langle \Psi | H | \Psi \rangle = E \langle \Psi | \Psi \rangle \) we obtain the expression:

\[ \sum_\beta \sum_\alpha C_\beta C_\alpha \langle \psi_\beta | H | \psi_\alpha \rangle = E \sum_\mu \sum_\nu C_\mu C_\nu \langle \psi_\mu | \psi_\nu \rangle \]
For any independent-coefficient variation, the following equation is derived (i.e. let all \(\delta C_\mu\) vanish except for one).

\[
\sum_\beta \sum_\alpha c_\beta c_\alpha \langle \psi_\beta | \psi_\alpha \rangle * \sum_\gamma \delta C_\mu c_\gamma \langle \psi_\mu | H | \psi_\gamma \rangle - \\
\sum_\rho \sum_\sigma c_\rho c_\sigma \langle \psi_\rho | H | \psi_\sigma \rangle * \sum_\zeta \delta C_\mu c_\zeta \langle \psi_\mu | \psi_\zeta \rangle = 0
\]

We use \(\langle \Psi | H | \Psi \rangle = E \langle \Psi | \Psi \rangle\) to rewrite the previous result involving the coefficient variations.

\[
\sum_\beta \sum_\alpha c_\beta c_\alpha \langle \psi_\beta | \psi_\alpha \rangle * \sum_\gamma \delta C_\mu c_\gamma \langle \psi_\mu | H | \psi_\gamma \rangle - \\
E \sum_\rho \sum_\sigma c_\rho c_\sigma \langle \psi_\rho | \psi_\sigma \rangle * \sum_\zeta \delta C_\mu c_\zeta \langle \psi_\mu | \psi_\zeta \rangle = 0
\]

After cancellation of common terms, this reduces to

\[
\sum_\gamma \delta C_\mu c_\gamma \langle \psi_\mu | H | \psi_\gamma \rangle - E \sum_\zeta \delta C_\mu c_\zeta \langle \psi_\mu | \psi_\zeta \rangle = 0
\]

Since this is true for any coefficient variation one obtains

\[
\sum_\gamma c_\gamma \langle \psi_\mu | H | \psi_\gamma \rangle - E \sum_\zeta c_\zeta \langle \psi_\mu | \psi_\zeta \rangle = 0
\]

Since \(\gamma\) and \(\zeta\) are dummy indices it is advantageous to group the terms as a summation over one index subscript. We cancel out the terms:

\[
\sum_\rho \sum_\sigma c_\rho c_\sigma \langle \psi_\rho | \psi_\sigma \rangle
\]

And arrive at

\[
\sum_\eta c_\eta \langle \psi_\mu | H | \psi_\eta \rangle - E \sum_\eta c_\eta \langle \psi_\mu | \psi_\eta \rangle = 0
\]

Define \(H_\mu := \langle \psi_\mu | H | \psi_\mu \rangle\) and \(S_\mu := \langle \psi_\mu | \psi_\mu \rangle\). In matrix form the secular equation may be rewritten as an operation on a column vector space with expansion coefficients from the LCAO.
\[(H_{\mu\nu} - E S_{\mu\nu})C_{\nu} = 0\]

For the nontrivial trial functions the entire C cannot vanish. Therefore, the operator must be singular forcing the following constraint:

\[\text{det} (H_{\mu\nu} - E S_{\mu\nu}) = 0\]  \hspace{1cm} (A.1)

The entry values of the matrix correspond to overlap integrals involving different atomic sites.

**A.2 Application to CdS**

For illustrative purposes, CdS will be analyzed. In the wurtzite configuration, CdS has two elements as a basis for the nanocrystal. We treat the nanocrystal as a composite of two nano sub lattices each with the HCP (figure A.4) configuration. The composite nano lattice is the result of two nano sub lattices displaced along the primitive axis that is perpendicular to the two dimensional hexagonal net giving the structure in figure A.5a.

![Figure A.4](image)

Figure A.4 a) HCP cell structure (blue) for sub lattice with S atom. b) HCP cell structure (red) for sub lattice with Cd atom.
In the molecular orbital framework, one works with a matrix with dimensions in at least in the hundreds when constructing the secular equation A.1. The result is a cumbersome determinant to compute and solve. Instead of doing a linear combination of atomic orbitals at every atomic site, here we will form a trial function from a linear combination of Bloch sums that satisfy periodic boundary conditions. The Bloch sum is constructed by applying the following projection operator to some atomic orbital $\psi_o$.

$$P^\mu = \frac{N_H}{N_D} \sum_{D}(\chi^{-1})^\mu U(D) = \frac{1}{N} \sum_{n=1}^{N} e^{-i\mathbf{k} \cdot \mathbf{r}_n} T_n \quad [53]$$

$$P^k \psi_o = \frac{1}{N} \sum_{n=1}^{N} e^{-i\mathbf{k} \cdot \mathbf{r}_n} T_n \psi_o(\mathbf{r}) \quad \text{k's run within first Brillouin zone} \quad [53]$$

$\mathbf{r}_n$'s are the primitive translation vectors

$$T_n \psi_o(\mathbf{r}) = \psi_o(\mathbf{r} + \mathbf{r}_n) \quad \text{but} \quad T_N \psi_o(\mathbf{r}) = \psi_o(\mathbf{r} + \mathbf{r}_N) = \psi_o(\mathbf{r})$$

Figure A.5 a) Wurtzite cell structure. b) Tetrahedral coordination of atoms from different HCP substructures.
\( r_N \) is measured from the center of the nanocrystal to the surface of the nanocrystal. The periodic boundary condition above is a generalization of a closed loop in 3D. With the CdS, there are four Bloch sums. Each Bloch sum corresponds to an atom type associated to each HCP. The determinant of the CdS dot then becomes an 8x8 for the \( p_x \) and \( p_y \) and a 4x4 for the s and a 4x4 for the \( p_z \) opposed to some 100x100 or even 1000x1000 matrix in molecular orbital theory. The remaining element of the analysis is the evaluation of the integrals. In the tight binding approximation, we look at nearest neighbors.

\[
H_{ij} = E_i \delta_{ij} + \sum_{\tilde{t}_l} e^{i \mathbf{k} \cdot \tilde{t}_l} \int \psi_i(\mathbf{r}) V_a(\mathbf{r} - \tilde{t}_l) \psi_j(\mathbf{r} - \tilde{t}_l) d\mathbf{r}
\]  

where the overlap integrals, \( S_{ij} \) from equation A.3 are approximated to \( \delta_{ij} \) and the \( t_l \)'s correspond to the first nearest neighbors.

The integrals will involve overlap of \( \psi \) between two atoms, Cd and S. For a two center overlap, the traditional spherical coordinates prove to be counterproductive. They involve three coordinates of one electron with respect to an atom 1 that are dependent of another three coordinates with respect to another atom 2. Here, prolate spheroid coordinates \[54] will be implemented to circumvent some of these obstacles posed by spherical coordinates. Since the prolate spheroidal coordinates are not as common as the traditional spherical and cylindrical curvilinear coordinates, details of the prolate spheroid coordinates will be presented here.

First the transformation from Cartesian to new coordinates:

\[
x = \frac{R}{2} \sin \alpha \sin \beta \cos \phi, \quad y = \frac{R}{2} \sin \alpha \sin \beta \sin \phi, \quad z = \frac{R}{2} \cosh \alpha \cos \beta
\]

R is defined as the distance between Cd and its nearest S atom.

After another transformation:
\( q = \cosh \alpha, \ \ p = \cos \beta, \ \ \phi = 0 \)

The second transformation from Cartesian to new coordinates:

\[
\begin{align*}
    x &= \frac{R}{2} \sqrt{q^2 - 1} \sqrt{1 - p^2} \cos \phi, \\
    y &= \frac{R}{2} \sqrt{q^2 - 1} \sqrt{1 - p^2} \sin \phi,
\end{align*}
\]

Volume integral element with \( h \) scale factors:

\[
d\vec{r} = h_q \, d\vec{q} + h_p \, d\vec{p} + h_{\phi} \, d\phi
\]

Gradient in prolate coordinates:

\[
\nabla \psi = \frac{1}{h_q} \, \frac{\partial \psi}{\partial q} + \frac{1}{h_p} \, \frac{\partial \psi}{\partial p} + \frac{1}{h_{\phi}} \, \frac{\partial \psi}{\partial \phi}
\]

Restatement of divergence theorem:

\[
\iiint_V (\nabla \cdot \nabla \psi) \, dV = \iint_S \nabla \psi \cdot dS
\]

Surface element integrals:

- Surface 1: \( d\vec{q} \, d\vec{p} \, d\phi \, \frac{\partial}{\partial q} \left( h_q \, h_p \, \frac{\partial \psi}{\partial \phi} \right) \)
- Surface 2: \( d\vec{q} \, d\vec{p} \, d\phi \, \frac{\partial}{\partial p} \left( h_p \, h_{\phi} \, \frac{\partial \psi}{\partial \phi} \right) \)
- Surface 3: \( d\vec{q} \, d\vec{p} \, d\phi \, \frac{\partial}{\partial q} \left( h_q \, h_{\phi} \, \frac{\partial \psi}{\partial \phi} \right) \)

Scale factors:

\[
h_q = \left| \frac{\partial \vec{r}}{\partial \vec{q}} \right| = \sqrt{\left( \frac{\partial x}{\partial q} \right)^2 + \left( \frac{\partial y}{\partial q} \right)^2 + \left( \frac{\partial z}{\partial q} \right)^2} = \sqrt{\frac{R^2 q^2 (1-p^2)}{4(q^2-1)} + \frac{R^2 p^2}{4}} = \sqrt{\frac{R^2 q^2 - R^2 p^2}{4(q^2-1)}}
\]

\[
h_p = \sqrt{\frac{R^2 q^2 - R^2 p^2}{4(1-p^2)}}, \quad h_{\phi} = \sqrt{\frac{R^2(q^2-1)(1-p^2)}{4}}
\]

From surface 1:

\[
\frac{R}{2} \frac{2p^2 q^2 - p^2}{(1-p^2)(q^2-1)} \frac{\partial^2 \psi}{\partial \phi^2}
\]

From surface 2:

\[
\frac{R}{2} (1-p^2) \frac{\partial^2 \psi}{\partial p^2} - 2p \frac{R}{2} \frac{\partial \psi}{\partial p}
\]

From surface 2:

\[
\frac{R}{2} (q^2 - 1) \frac{\partial^2 \psi}{\partial q^2} + 2q \frac{R}{2} \frac{\partial \psi}{\partial q}
\]

Laplacian:

\[
(\nabla \cdot \nabla \psi) h_q h_p h_{\phi} \, d\vec{q} \, d\vec{p} \, d\phi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \\
\begin{bmatrix}
    \frac{R}{2} (1-p^2) \frac{\partial^2 \psi}{\partial p^2} - 2p \frac{R}{2} \frac{\partial \psi}{\partial p} + \frac{R}{2} (q^2 - 1) \frac{\partial^2 \psi}{\partial q^2} + 2q \frac{R}{2} \frac{\partial \psi}{\partial q} + \frac{R}{2} \frac{q^2 - p^2}{(1-p^2)(q^2-1)} \frac{\partial^2 \psi}{\partial \phi^2}
\end{bmatrix} \times \frac{8}{R^3(q^2-p^2)}
\]

(A.6)
The constraint relation for the cartesian coordinates gives:

\[
\frac{z^2}{\left(\frac{R}{2}\right)^2 q^2} + \frac{x^2}{\left(\frac{R}{2}\right)^2 p^2} + \frac{y^2}{\left(\frac{R}{2}\right)^2 p^2} = 1
\]

From this it is obvious that \(\frac{R}{2}\) must be the distance from the origin to one of the foci. The sum of the two distances from a point on the ellipsoid and the foci must therefore be \(qR\) [54]:

\[
qR = r_1 + r_2
\]  \hspace{1cm} (A.7)

The second constraint relation for the cartesian coordinates gives:

\[
\frac{z^2}{\left(\frac{R}{2}\right)^2 p^2} - \frac{x^2}{\left(\frac{R}{2}\right)^2 p^2} - \frac{y^2}{\left(\frac{R}{2}\right)^2 p^2} = 1
\]

The difference of the two distances from a point on the hyperboloid and the foci must \(pR\)

\[
pR = r_1 - r_2
\]  \hspace{1cm} (A.8)

The distances \(r_1\) and \(r_2\) are depicted in figure A.9 for the ellipsoid and hyperboloid case.

A.9 demonstrates the relation of the two nearest atoms and the geometry of the new coordinates.

![Diagram](image1)

Figure A.9 In dealing with the nearest neighbor's approximation, we deal with the two body problem. A change in coordinates to the prolate spheroidal coordinates results in the two centers of the system as foci of an ellipsoid and hyperboloid.
For the direction cosines

\[
\cos \theta_1 = \frac{z_1}{|r_1|} = \sqrt{\frac{(q+p)^2-(q^2-1)(1-p^2)}{q+p}} = \frac{qp+1}{q+p}
\]

(A.9)

\[
\cos \theta_2 = \frac{z_2}{|r_2|} = \sqrt{\frac{(q-p)^2-(q^2-1)(1-p^2)}{q-p}} = \frac{1-qp}{q-p}
\]

(A.10)

With these coordinates, we can recast the following Slater orbitals [1,54]

\[
\psi = \frac{(2\xi_\alpha)^{n_\alpha+1/2}}{\sqrt{(2n_\alpha)!}} \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} r^{n_\alpha-1} e^{-\xi_\alpha r} P_l^m (\cos \theta)
\]

(A.11)

into the prolate coordinate representation. These will serve as the atomic orbitals to form the appropriate Bloch sums. With all these details, we use the appropriate quadrature to evaluate the energy levels as described in the Matlab code of this appendix. The results of the tight binding implementation are illustrated in figures A.10 to A.14. Observe that the sample size corresponds to the number of primitive cells forming the CdS nanocrystal which in turn relates to the number of atoms forming the sample volume. The larger the atom number is the closer the electronic energy levels become. The figures from A.10 to A.14 illustrate the transition from atomic like electronic energy levels to a band which is associated with a solid state. Figure A.11 in particular is analogous to the HOMO – LUMO level diagrammed in figure 1.1
Figure A.10 Energy state profile for wurtzite consisting of CdS. The tight binding simulation was for 64 primitive cells about 320 atoms. Energy is in electron volts.

Figure A.11 Energy state profile for wurtzite consisting of CdS. The tight binding simulation was for 1000 primitive cells about 5000 atoms. Energy is in electron volts.
Figure A.12 Energy state profile for wurtzite consisting of CdS. The tight binding simulation was for 27000 primitive cells about 135000 atoms. Energy is in electron volts.

Figure A.13 emphasizes the energy dispersion in a particular $k$ direction for a large cluster of CdS atoms. One already sees the general band structure that is eventually realized when dealing with an arbitrarily large number as illustrated in figure A.14. From these considerations, one can interpret nanocrystals as a transition from molecules to condensed matter.

Figure A.13 Energy state profile for a particular molecular orbital set for wurtzite consisting of CdS. The tight binding simulation was for 1000 primitive cells about 5000 atoms. Energy is in electron volts.
Figure A.14 Energy state profile for a particular molecular orbital set for wurtzite consisting of CdS. The tight binding simulation was for 27000 primitive cells about 135000 atoms. Energy is in electron volts.
Appendix B

B.1 Electron Beam Lithography

Part of the fabrication techniques in implementing colloidal quantum dots involved electron beam lithography. This section shows the general procedural flow for this method. The primary lithographic resists that were used were SU-8 and PMMA. SU-8 is an organic photo-resistive material that when exposed to radiation becomes insoluble (negative resist) to a particular solvent. After the solvent is applied, a pattern emerges. If the resist is positive, such as PMMA, the part of the resist exposed to radiation is washed away leaving a pattern of “windows” (these “windows” expose the underlying substrate that the resist was deposited on). Whereas if the resist were negative, the resist that was exposed remains and the part that wasn’t exposed washes away leaving the bare substrate. The radiation that is implemented is an electron beam from a Scanning Electron Microscope, (SEM). A potential difference in a vacuum between an electrode and a sharp point where the electron will be emitted from is established. This is the source for generating an electron beam inside the SEM. With the SEM, electron beam lithography is done by using electromagnetic coils to deflect the electron beam and utilizing a beam blanker to control when the beam writes or does not write. This is controlled by the Nanometer Pattern Generation System, (NPGS) developed by Joe Nabity, Ph.D. Before the writing is done, the microscope must be optimized by focusing the beam onto a working plane that is comparable to the working distance of the actual writing. The objective is to match the confocal parameter of the beam with the thickness of the sample (figure B.1). We optimize the microscope by reducing astigmatism on a
sample of sputtered gold with critical features smaller than the critical features of the
device we are attempting to fabricate.

![Electron beam](image)

**Figure B.1.** The beam should not spread out too much within the resist thickness to get
optimal side walls and best resolution between coupled devices.

During the writing period, the beam must “dwell” within a given area of the entire
structure to be written. This exposure time is a function of the area, area dosage, and
beam current which is measured by a faraday cup on the same stage as the sample to be
written on. The area is equal to the center–to–center spacing multiplied by the line
spacing. The center-to-center distance is the distance between two adjacent beam
exposure spots. The line spacing is the distance between the rows of exposure spots. This
is comparable to pixels within a given line scan. The separation between scan lines is the
line spacing. And the spacing between pixels is the center-to-center distance.

For an array of bent waveguides as shown is the CAD in figure B.2, we use a beam
current of 10 picoamps, a line spacing of 45.78 nm and center to center distance of
45.78nm in an area of 2714 by 2708 microns of the array within a 2715 by 2715 writing field. Using the formula:

\[
\text{Exposure time} = \frac{\text{Area} \times \text{Area dosage}}{\text{Beam current}} \quad [55]
\]

This gives an exposure time of 4.191 micro seconds for each area constituent of the entire array of bent waveguides.

Figure B.2. (a) CAD design of array of bent waveguides using DesignCAD16 Express. The design CAD express file is ported to the Nano pattern generating software for electron beam lithography. (b) The software controls the scanning electron microscope with a 16 bit digital analog converter to control x and y scan coils for deflection of electron beam within a writing field [55]. (c) CAD design of figure B.2a has attached protocols for serpentine sweep of electron beam on surface in order to fill the polygon that is to be exposed on the surface of the substrate.
B.2 Alignment Marks

In order to integrate active material to passive components, patterns have to be created that will serve as markers. These are needed during the alignment stages of the electron beam writing process. First we do the standard electron beam lithography with SU-8 resist that has a kinematic viscosity of 45 cSt. We pattern 5 μm thick crosses that are within a 25 μm² area (figure B.3).

![Cross marks on top of silicon substrate made by electron beam lithography. The cross marks are approximately 5 microns thick.](image)

Figure B.3. Cross marks on top of silicon substrate made by electron beam lithography. The cross marks are approximately 5 microns thick.

After the cross marks are patterned, a less viscous resist is deposited on the entire sample. The resist we use is PMMA with 4% chlorobenzene. The deposited resist is about 300 nm thick. Spin coating deposits most of the resist between the patterns and thins out on top of them (figure B.4).

![Patterned cross marks on top of silicon substrate with spin coated PMMA. Spin coating forces most of the resist to deposit on larger surface areas of the substrate and less on the patterned resist.](image)

Figure B.4. Patterned cross marks on top of silicon substrate with spin coated PMMA. Spin coating forces most of the resist to deposit on larger surface areas of the substrate and less on the patterned resist.
We sputter about 80nm of gold on top of the entire sample (figure B.5).

Figure B.5. Gold is sputtered on entire sample. Thickness of gold film is not drawn to scale. Film is actually about ¼ the thickness of the PMMA resist.

The gold film is not continuous, however. There is a discontinuity of gold at the edges of the SU-8 cross marks. We take advantage of this separated gold by doing a lift-off process as illustrated in figure B.6.

Figure B.6. The sample is immersed in a dish of acetone. The PMMA lifts-off the substrate removing the gold that is not attached to the gold deposited on the cross marks.

As we stir the sample in the acetone, we also rinse the sample with acetone so that only gold remains on the cross marks (figure B.7).

Figure B.7. The thin film gold survives on the patterned devices. Most of gold is removed from the rest of the entire sample.
The final result is alignment marks (figure B.8) that we can see when using the SEM to scan for positions to write the waveguides.

Figure B.8. Gold alignment marks made for integration of active waveguides to passive waveguide components.

While scanning for the gold-cross alignment marks, the sample is exposed by the electron beam. To prevent unwanted patterns from be created during the scanning process, we make a geometry, such as an arrow, at the edge of the sample. This arrow locator will also be covered in gold after the lift-off process. The arrow must be placed at a precise location on the sample. We would create the first alignment mark with respect to the arrow. Any other alignment marks that are created are then measured with respect to the preceding alignment mark. When we have deposited the resist to do the lithography, we zoom to the edge of the sample. From there we locate the alignment arrow. Once we have found it, we blank the beam and move the writing field to the first alignment mark to be scanned. The beam may not necessarily hit the alignment mark dead on. There might be an offset by a few microns. We then scan a few microns to the left and right as well as top and bottom but far enough away from the area where the actual device is to be made. This process continues with the next alignment mark.
B.3 Alignment Method

As stated previously we need to scan the gold alignment marks away from the area the actual writing is done. First we position the sample to the writing field were we assume there are alignment marks are as depicted in figure B.9. Then we use the align scan protocols of the alignment program in the NPGS where we scan a much smaller writing field for the alignment marks as in figure B.10.

Figure B.9. Gold alignment marks within writing field electron beam writing.

Figure B.10. Scanning of smaller surface to locate alignment marks.
Once we have found the alignment marks we then write the passive wave guide structures in an arrangement illustrated in figure B.11.

Figure B.11. Passive waveguides aligned via alignment marks.

Before we can integrate the active components to the passive waveguides, we had to remove the sample and develop it to produce the patterns shown in figure B.11. Then we would have to prepare the sample with the active resist and then place it back into the SEM. We then have to find the alignment arrow once again in order to locate where the alignment marks are. Once the sample is placed in position as in B.9 we scan again for the alignment marks (figure B.12).

Figure B.12. Scanning to locate alignment marks for second lithography.
After the second scan we do the electron beam lithography with the active resist to integrate the active structure to the passive components as shown in figure B.13.

Figure B.13. Active waveguide aligned via alignment marks.
Appendix C

Matlab Code

C.1 Tightbinding

Function subroutines for evaluating spherical harmonics:

```matlab
function value=legendre_derv(p,l,m,direct_cosine)
x=direct_cosine;
m=abs(m);
if l==0
    value=0;
elseif m==0 & l>0
    value=(1./(2*sqrt(1-x.^2))).*(p(2,:)-(l*(l+1)*factorial(l+1)/factorial(l-1))*p(2,:));
elseif (m+2)<=l+1 & m~=0
    value=(1./(2*sqrt(1-x.^2))).*(p(m+2,:)-(l+m)*(l-m+1)*p(m,:));
elseif m+2>l+1
    value=(1./(2*sqrt(1-x.^2))).*((l+m)*(l-m+1)*p(m,:));
end

function value=legendre_secondderiv(p,l,m,direction_cosine)
x=direction_cosine;
m=abs(m);
if (l==1 & m==0)
    value=0;
elseif ((m+2)<=(l+1))
    value=(1./(2*sqrt(1-x.^2))).*(legendre_derv(p,l,m+1,direction_cosine)-(l+m)*(l-m+1)*legendre_derv(p,l,m-1,direction_cosine)+(x./(2*(1-x.^2).^3/2)))*((l+m)*(l-m+1)*p(m,:));
elseif l~=0
    value=(1./(2*sqrt(1-x.^2))).*((l+m)*(l-m+1)*legendre_derv(p,l,m-1,direction_cosine)+(x./(2*(1-x.^2).^3/2)))*((l+m)*(l-m+1)*p(m,:));
else
    value=0;
end

function value=dx1_dp(q,p)
value=((1+q.*p)./(q-p).^2)+q./(q-p);  

function value=dx1_dq(q,p)
value=((1+q.*p)./(q-p).^2)+p./(q-p);  

function value=dx1x1_dpdp(q,p)
value=(2*(1+q.*p)./(q-p).^3)-2*q./(q-p).^2;  

function value=dx1x1_dpdq(q,p)
value=(2*(1+q.*p)./(q-p).^3)+(-1*(q+p)./(q-p).^2)+(1./(q+p));  

function value=dx1x1_dqdq(q,p)
value=(2*(1+q.*p)./(q-p).^3)-2*p./(q-p).^2;  

function value=dx2_dp(q,p)
value=((1-q.*p)./(q-p).^2)-q./(q-p);  
```
function value=dx2_dq(q,p)
value=((-1-q.*p)./(q-p).^2)-p./(q-p);

function value=dx2x2_dpdp(q,p)
value=(2*(1-q.*p)./(q-p).^3)-2*q./(q-p).^2;

function value=dx2x2_dpdq(q,p)
value=(2*(1-q.*p)./(q-p).^3)+(1*(q+p)./(q-p).^2)-(1./(q-p));

function value=dx2x2_dqdq(q,p)
value=(-2*(1-q.*p)./(q-p).^3);

function Y = spericalharmonic(l,m,direct_cosine,phi)
p=legendre(l,direct_cosine);
if m >= 0
   Y=(((-1)^m)*(sqrt(((2*l+1)/(4*pi))*(factorial(l-m)/factorial(l+m))))*p(m+1,:).*exp(1i*m*phi));
else m<0
   m=-m;
   Y=(((-1)^m)*(sqrt(((2*l+1)/(4*pi))*(factorial(l-m)/factorial(l+m))))*(-1i)*m*p(m+1,:).*exp(-1i*m*phi));
end

function Y = spericalharmonic_dervphi(l,m,direction_cosine,phi)
p=legendre(l,direction_cosine);
if m >= 0
   Y=(((-1)^m)*(sqrt(((2*l+1)/(4*pi))*(factorial(l-m)/factorial(l+m))))*1i*m*p(m+1,:).*exp(1i*m*phi));
else m<0
   m=-m;
   Y=(((-1)^m)*(sqrt(((2*l+1)/(4*pi))*(factorial(l-m)/factorial(l+m))))*(-1i)*m*p(m+1,:).*exp(-1i*m*phi));
end

function Y = spericalharmonic_dervtheta(l,m,direct_cosine,phi)
p=legendre(l,direct_cosine);
if m >= 0
   Y=(((-1)^m)*(sqrt(((2*l+1)/(4*pi))*(factorial(l-m)/factorial(l+m))))*legendre_derv(p,l,m,direct_cosine).*exp(1i*m*phi));
else m<0
   m=-m;
   Y=(((-1)^m)*(sqrt(((2*l+1)/(4*pi))*(factorial(l-m)/factorial(l+m))))*legendre_derv(p,l,m,direct_cosine).*exp(-1i*m*phi));
end

function Y = spericalharmonic_secondderivphi(l,m,theta,phi)
p=legendre(l,cos(theta));
if m >= 0
   Y=(((-1)^m)*(sqrt(((2*l+1)/(4*pi))*(factorial(l-m)/factorial(l+m))))*1i*m^2*p(m+1,:).*exp(1i*m*phi));
else m<0
   m=-m;
   Y=(((-1)^m)*(sqrt(((2*l+1)/(4*pi))*(factorial(l-m)/factorial(l+m))))*1i*m^2*p(m+1,:).*exp(-1i*m*phi));
end
function $Y = \text{sphericalharmonic} \_\text{seconddervtheta}(l,m,\text{direction} \_\text{cosine},\phi)$

$p = \text{legendre}(l,\text{direction} \_\text{cosine})$;

if $m \geq 0$
    $Y = ((-1)^m) \sqrt{((2l+1)/(4\pi)) *(\text{factorial}(l-m)/\text{factorial}(l+m)))} \times \text{legendre} \_\text{secondderv}(p,l,m,\text{direction} \_\text{cosine}). \times (\exp(1i \times m \times \phi))$;
elseif $m < 0$
    $m = -m$;
    $Y = ((-1)^m) \sqrt{((2l+1)/(4\pi)) *(\text{factorial}(l-m)/\text{factorial}(l+m)))} \times \text{legendre} \_\text{secondderv}(p,l,m,\text{direction} \_\text{cosine}). \times (\exp(-1i \times m \times \phi))$;
end

function value=orbital(x, direction_cosine, phi)
switch x
    case 0
        value=sphericalharmonic(x,x,direction_cosine,phi);
    case 1
        value=(sphericalharmonic(x,x,direction_cosine,phi)+ sphericalharmonic(x,-x,direction_cosine,phi))/2;
    case 2
        value=(sphericalharmonic(x,x,direction_cosine,phi)- sphericalharmonic(x,-x,direction_cosine,phi))/2i;
end

function value=orbital\_dervphi(x, direction_cosine, phi)
switch x
    case 0
        value=sphericalharmonic\_dervphi(x,x,direction_cosine,phi);
    case 1
        value=(sphericalharmonic\_dervphi(x,x,direction_cosine,phi)+ sphericalharmonic\_dervphi(x,-x,direction_cosine,phi))/2;
    case 2
        value=(sphericalharmonic\_dervphi(x,x,direction_cosine,phi)- sphericalharmonic\_dervphi(x,-x,direction_cosine,phi))/2i;
end

function value=orbital\_dervtheta(x, direction_cosine, phi)
switch x
    case 0
        value=sphericalharmonic\_dervtheta(x,x,direction_cosine,phi);
    case 1
        value=(sphericalharmonic\_dervtheta(x,x,direction_cosine,phi)+ sphericalharmonic\_dervtheta(x,-x,direction_cosine,phi))/2;
    case 2
        value=(sphericalharmonic\_dervtheta(x,x,direction_cosine,phi)- sphericalharmonic\_dervtheta(x,-x,direction_cosine,phi))/2i;
end

function value=orbital\_seconddervphi(x, direction_cosine, phi)
switch x
    case 0
        value=sphericalharmonic\_seconddervphi(x,x,direction_cosine,phi);
    case 1
        value=(sphericalharmonic\_seconddervphi(x,x,direction_cosine,phi)+ sphericalharmonic\_seconddervphi(x,-x,direction_cosine,phi))/2;
    case 2
function value=orbital_seconddervtheta(x,direction_cosine,phi)
switch x
    case 0
        value=sphericalharmonic_seconddervtheta(x,x,direction_cosine,phi);
    case 1
        value=(sphericalharmonic_seconddervtheta(x,x,direction_cosine,phi)+
sphericalharmonic_seconddervtheta(x,-x,direction_cosine,phi))/2;
    case 2
        value=(sphericalharmonic_seconddervtheta(x,x,direction_cosine,phi)-
sphericalharmonic_seconddervtheta(x,-x,direction_cosine,phi))/2i;
end

function value=orbital2(x,direct_cosine,phi)
switch x
    case 0
        value=sphericalharmonic(x+1,x,direct_cosine,phi);
    case 1
        value=(sphericalharmonic(x,x,direct_cosine,phi)+
sphericalharmonic(x,-x,direct_cosine,phi))/2;
    case 2
        value=(sphericalharmonic(x,x,direct_cosine,phi)-
sphericalharmonic(x,-x,direct_cosine,phi))/2i;
end

function value=orbital2_dervtheta(x,direction_cosine,phi)
switch x
    case 0
        value=sphericalharmonic_dervtheta(x+1,x,direction_cosine,phi);
    case 1
        value=(sphericalharmonic_dervtheta(x,x,direction_cosine,phi)+
sphericalharmonic_dervtheta(x,-x,direction_cosine,phi))/2;
    case 2
        value=(sphericalharmonic_dervtheta(x,x,direction_cosine,phi)-
sphericalharmonic_dervtheta(x,-x,direction_cosine,phi))/2i;
end

function value=orbital2_dervphi(x,direction_cosine,phi)
switch x
    case 0
        value=sphericalharmonic_dervphi(x+1,x,direction_cosine,phi);
    case 1
        value=(sphericalharmonic_dervphi(x,x,direction_cosine,phi)+
sphericalharmonic_dervphi(x,-x,direction_cosine,phi))/2;
    case 2
        value=(sphericalharmonic_dervphi(x,x,direction_cosine,phi)-
sphericalharmonic_dervphi(x,-x,direction_cosine,phi))/2i;
end

function value=orbital2_seconddervphi(x,direction_cosine,phi)
switch x
    case 0
        value=sphericalharmonic_seconddervphi(x+1,x,direction_cosine,phi);
case 1
value=(sphericalharmonic_seconddervphii(x,x,direction_cosine,phi)+
sphericalharmonic_seconddervphii(x,-x,direction_cosine,phi))/2;
case 2
value=(sphericalharmonic_seconddervphii(x,x,direction_cosine,phi)-
sphericalharmonic_seconddervphii(x,-x,direction_cosine,phi))/2i;
end

function value=orbital2_seconddervtheta(x,direction_cosine,phi)
switch x
    case 0
        value=sphericalharmonic_seconddervtheta(x+1,x,direction_cosine,phi);
    case 1
        value=(sphericalharmonic_seconddervtheta(x,x,direction_cosine,phi)+
sphericalharmonic_seconddervtheta(x,-x,direction_cosine,phi))/2;
    case 2
        value=(sphericalharmonic_seconddervtheta(x,x,direction_cosine,phi)-
sphericalharmonic_seconddervtheta(x,-x,direction_cosine,phi))/2i;
end

IMPLEMTATION OF EQUATION (A.10)
function value=radial(r,l_a,n_a,l,m)
    value=((2*l_a )^(n_a+.5))/sqrt(factorial(2*n_a))* sqrt((2*l+1)*factorial(l-
m)/2*factorial(l+m)) * r.^(n_a-1).* exp(-l_a* r);

function value=radial_derv(r,l_a,n_a,l,m)
    value=((2*l_a )^(n_a+.5))/sqrt(factorial(2*n_a))* sqrt((2*l+1)*factorial(l-
m)/2*factorial(l+m)) *(l_a^2)*r.^(n_a-1).* exp(-l_a* r)+(n_a-2)* r.^(n_a-2).* exp(-l_a* r));

function value=radial_secondderv(r,l_a,n_a,l,m)
    value1=((2*l_a )^(n_a+.5))/sqrt(factorial(2*n_a))* sqrt((2*l+1)*factorial(l-
m)/2*factorial(l+m))*(l_a^2)*r.^(n_a-1).* exp(-l_a* r)-l_a*(n_a-1)* r.^(n_a-2).* exp(-l_a* r));
    value2=((2*l_a )^(n_a+.5))/sqrt(factorial(2*n_a))* sqrt((2*l+1)*factorial(l-
m)/2*factorial(l+m))*(n_a-2)*(n_a-1)* r.^(n_a-3).* exp(-l_a* r)-l_a*(n_a-1)* r.^(n_a-2).* exp(-l_a* r));
    value=value1+value2;

function value=kinetic_value(q,p,phi)
hbar=1.054571726e-34;
mass=9.10938215e-31;
Cd=5;
S=3;
o=0;
l_a=1;
n_a=S;
l=0;
m=0;
 percentage_cosine=cos_beta*(1+q.*p)./(q+p)+sqrt(1-cos_beta^2)*((q.*p)^2)/(q+p)^2;
 percentage_cosine=cos_beta*(1-q.*p)./(q-p)+sqrt(1-cos_beta^2)*((q.*p)^2)/(q-p)^2;
 percentage_cosine=cos(p);
 percentage_cosine=(1+q.*p)./(q+p); ("*THESE ARE UNCOMMENTED FOR THE
 APPROPRIATE COSINE INTEGRALS DERIVED FROM EQUATIONS (A.8) AND (A.9)
 USED IN THE TWO-CENTER INTEGRALS *")

direction_cosine=(1-q.*p)./(q-p);
c=.6749e-9;
a=.4135e-9;
u=0.25;

%THE d's ARE THE DISPLACEMENTS OF ATOMS ASSOCIATED WITH A LATTICE POINT IN THE WURTZITE STRUCTURE:

d1=[0 0 0];
d2=[0 0 c*u];
d4=[0 a/sqrt(3) c*(.5+u)];
d3=[0 a/sqrt(3) c*.5];
R=sqrt(dot((d4-d3),(d4-d3)));
R=sqrt(dot((d3-d2),(d3-d2)));
%cos_beta=(R/(d3-d2));

r=(q-p)/2*R; %from equation (A.6) and (A.7)

%IMPLEIMENTATION OF EQUATION (A.5):

function value=kinetic2_value(q,p,phi)

\[ hbar = 1.054571726e-34; \]
\[ mass = 9.10938215e-31; \]
\[ C_d = 5; \]
\[ S = 3; \]
\[ o = 0; \]
\[ l_a = 1; \]
\[ n_a = S; \]
\[ l = 1; \]
\[ m = 0; \]

%direction_cosine=cos_beta*(1+q.*p)./(q+p)+sqrt(1-cos_beta^2)*((q.^2)+(p.^2)-1-\( q.*p \).^2)/(q+p).^2);
%direction_cosine=cos_beta*(1-q.*p)./(q-p)+sqrt(1-cos_beta^2)*((q.^2)+(p.^2)-1-\( q.*p \).^2)/(q-p).^2);
%direction_cosine=(1+q.*p)./(q+p);
%direction_cosine=(1-q.*p)./(q-p);
c=.6749e-9;
a=.4135e-9;
u=.25;
d1=[0 0 0];
d2=[0 0 c*u];
d4=[0 a/sqrt(3) c*(.5+u)];
d3=[0 a/sqrt(3) c*.5];
%R=sqrt(dot((d4-d3),(d4-d3)));
R=sqrt(dot((d3-d2),(d3-d2)));
Rz=(d3-d2);
cos_beta=Rz(3)/R;
direction_cosine=cos_beta*(1-q.*p)./(q-p)+sqrt(1-cos_beta^2)*(((q.^2)+(p.^2)-1-(q.*p).^2)./(q-p).^2);
%r=(q+p)/2*R;

function value=kinetic3_value(q,p,phi)
hbar=1.054571726e-34;
mass=9.10938215e-31;
Cd=5;
S=3;
o=0;
l_a=1;
n_a=S;
l=0;
m=0;
direction_cosine=cos(p);
%direction_cosine=(1+q.*p)./(q-p);
%direction_cosine=(1-q.*p)./(q-p);
c=.6749e-9;
a=.4135e-9;
u=.25;
d1=[0 0 0];
d2=[0 0 c*u];
d4=[0 a/sqrt(3) c*(.5+u)];
d3=[0 a/sqrt(3) c*.5];
%R=sqrt(dot((d4-d3),(d4-d3)));  
%R=sqrt(dot((d3-d2),(d3-d2)));  
%r=(q+p)/2*R;
%r=(q-p)/2*R;
% THIS IS IMPLEMENTATION OF USUAL DIFFERENTIAL EQUATION IN SPHERICAL
% CoORDINATES
r=q;

d_p=-(direction_cosine./r).^2).*radial(r,l_a,n_a,l,m).*orbital_dervtheta(o,direction_cosine,phi);

dd_pp=(r.^-2).*radial(r,l_a,n_a,l,m).*(-direction_cosine.*orbital_dervtheta(o,direction_cosine,phi)+(sin(p).^2).*orbital_seconddervtheta(o,direction_cosine,phi));

t_p=dd_pp+d_p;

d_q=(2./r).*radial_derv(r,l_a,n_a,l,m).*orbital(o,direction_cosine,phi);

dd_qq=orbital(o,direction_cosine,phi).*radial_secondderv(r,l_a,n_a,l,m);

t_q=dd_qq+d_q;

t_phi=1./(r.*sin(p).^2).*orbital_secondddervphi(o,direction_cosine,phi).*radial(r,l_a,n_a,l,m);

value=-(hbar^2)/(2*mass)*(t_p+t_q+t_phi);

function value=kinetic4_value(q,p,phi)

hbar=1.054571726e-34;
mass=9.10938215e-31;
Cd=5;
S=3;
o=0;
l_a=1;
n_a=Cd;
l=1;
m=0;
direction_cosine=cos(p);
%direction_cosine=(1+q.*p)./(q+p);
%direction_cosine=(1-q.*p)./(q-p);
c=.6749e-9;
a=.4135e-9;
u=.25;
d1=[0 0 0];
d2=[0 0 c*u];
d4=[0 a/sqrt(3) c*(.5+u)];
d3=[0 a/sqrt(3) c*.5];  
%R=sqrt(dot((d4-d3),(d4-d3)));  
%R=sqrt(dot((d3-d2),(d3-d2)));  
%r=(q+p)/2*R;
%r=(q-p)/2*R;

r=q;

d_p=-(direction_cosine./r).^2).*radial(r,l_a,n_a,l,m).*orbital2_dervtheta(o,direction_cosine,phi);

dd_pp=(r.^-2).*radial(r,l_a,n_a,l,m).*(-direction_cosine.*orbital2_dervtheta(o,direction_cosine,phi)+(sin(p).^2).*orbital2_seconddervtheta(o,direction_cosine,phi));

t_p=dd_pp+d_p;

d_q=(2./r).*radial_derv(r,l_a,n_a,l,m).*orbital2(o,direction_cosine,phi);

dd_qq=orbital2(o,direction_cosine,phi).*radial_secondderv(r,l_a,n_a,l,m);
t_q=dd_qq+d_q;
t_phi=1./((r*sin(p)).^2).*orbital2_seconddervphi(o,direction_cosine,phi).*radial(r_l_a,n_a_l_m);
value=(-(hbar^2)/(2*mass))*(t_p+t_q+t_phi);

function value=potential(q,p,phi)
%direction_cosine=(1-q.*p)./(q-p);
%direction_cosine=(1+q.*p)./(q+p);
c=.6749e-9;
a=.4135e-9;
u=.25;
d4=[0 a/sqrt(3) c*(.5+u)];
d3=[0 a/sqrt(3) c*.5];
d1=[0 0 0];
d2=[0 0 c*u];
R=sqrt(dot((d4-d3),(d4-d3)));
%R=sqrt(dot((d3-d2),(d3-d2)));
Cd_Z=48;
S_Z=16;
e_0=8.854187817e-12;
e=1.602176565e-19;
%r=(q+p)./(2*R);
r=(q-p)./(2*R);
%r=q;
%value=(-Cd_Z*(e^2))./(e_0*4*pi*r);
value=(-S_Z*(e^2))./(e_0*4*pi*r);
%value=(-S_Z*(e^2))./(e_0*sqrt(((r.^2)+(R^2)-2*R*r.*direction_cosine)));

function value=product(x,y,z)
Cd=5;
S=3;
n_1=Cd;
n_2=S;
c=.6749e-9;
a=.4135e-9;
u=.25;
d4=[0 a/sqrt(3) c*(.5+u)];
d3=[0 a/sqrt(3) c*.5];
d1=[0 0 0];
d2=[0 0 c*u];
R=sqrt(dot((d4-d3),(d4-d3)));
%R=sqrt(dot((d3-d2),(d3-d2)));
%Rz=(d3-d2);
%cos_beta=Rz(3)/R;
%value=
radial(((y+x)/2*R),1,n_1,0,0).*orbital2(0,1+x.*y)./(x+y,z).*kinetic2_value(x,y,z)+
radial(((y+x)/2*R),1,n_1,0,0).*orbital2(0,1+x.*y)./(x+y,z).*potential(x,y,z).*orbital2(0,cos_beta^2)*((x.*y)/2+y.^2)^2./(x-y).^2);
\[ \text{value} = \text{radial}((y+x)/2^R,1,n_{1,0},0) \times \text{orbital}(0,(1+x \cdot y)/(x+y),z) \times \text{kinetic}_\text{value}(x,y,z) + \text{radial}((y+x)/2^R,1,n_{1,0},0) \times \text{orbital}(0,(1+x \cdot y)/(x+y),z) \times \text{potential}(x,y,z) \times \text{orbital}(0,(1-x \cdot y)/(x+y),z) \times \text{radial}((x-y)/2^R,1,n_{2,0},0) \]

\[ \text{value} = \text{radial}((y+x)/2^R,1,n_{1,0},0) \times \text{orbital}(0,(1+x \cdot y)/(x+y),z) \times \text{potential}(x,y,z) \times \text{orbital}(0,(1-x \cdot y)/(x+y),z) \times \text{radial}((x-y)/2^R,1,n_{2,0},0) \]

\[ \text{value} = \text{radial}((y+x)/2^R,1,n_{1,0},0) \times \text{orbital}_2(0,(1+x \cdot y)/(x+y),z) \times \text{kinetic}_4\_\text{value}(x,y,z) + \text{radial}((y+x)/2^R,1,n_{1,0},0) \times \text{orbital}_2(0,(1+x \cdot y)/(x+y),z) \times \text{potential}(x,y,z) \times \text{orbital}(0,(1-x \cdot y)/(x+y),z) \times \text{radial}((x-y)/2^R,1,n_{2,0},0) \]

\[ \text{triplequad('product',1,100000000000,-.9,.9,0,2*pi)} \]
%TIGHT BINDING APPROXIMATION SIMULATION

%LATTICE SPACING PARALLEL TO PRINCIPAL AXIS OF WURTZITE

c=.6749e-9;

%LATTICE SPACING PERPENDICULAR TO PRINCIPAL AXIS OF WURTZITE

a=.4135e-9;

volume=.5*c*(a^2)*sqrt(3);

%PRIMITIVE TRANSLATION VECTORS FOR HCP LATTICE

t1=a*[1/2 sqrt(3)/2 0];
t2=a*[-1/2 sqrt(3)/2 0 ];
t3=c*[0 0 1];

%RECIPROCAL LATTICE VECTORS

k1=(2*pi/volume)*cross(t2,t3);
k2=(2*pi/volume)*cross(t3,t1);
k3=(2*pi/volume)*cross(t1,t2);

%ATOMIC AND HOPING INTEGRALS

CE_ss=-1.4703e-027;
CE_pzpz=-3.7198e-027;
SE_ss=-1.5438e-021;
SE_pzpz=-3.9057e-021;
HCds_Ss_principal=-0.3606;
HSs_Cds_principal=HCds_Ss_principal;
HCds_Ss=-0.0424;
HSs_Cds=HCds_Ss;
HCds_Spz_principal=2.0533e-11;
HSpz_Cds_principal=HCds_Spz_principal;
HCds_Spz=-0.0758;
HSpz_Cds=HCds_Spz;
HCdpz_Ss_principal=1.1967e-11;
HSs_Cdpz_principal=HCdpz_Ss_principal;
HCdpz_Ss=-0.0758;
HSs_Cdpz=HCdpz_Ss;
HCdpz_Spz_principal=0.8763;
HSpz_Cdpz_principal=HCdpz_Spz_principal;
HCdpz_Spz=-0.1847;
HSpz_Cdpz=HCdpz_Spz;

%FINITE GROUP ORDER IN TRANSLATION

N=20 ;%N=4,N=10,N=30 (CUBE POWER GIVES PRIMITIVE CELL NUMER IN NANOCRYSTAL)

%MATRIX TO BE USED IN SECULAR EQUATION (A.3) INTIALIZATION

for u=1:4
    for v=1:4
        m(u,v)=0;
    end
end

for u=1:4
    for v=1:4
        M(u,v)=0;
    end
end
%MATRICE ASSIGNMENT

sign=1;
hold on
for g=-N/2:N/2
  k=((k2/N)*g);
  m(1,3)=HCds_Ss_principal;
  m(3,1)=HSs_Cds_principal;
  m(2,3)=HCds_Ss*(1+exp(1i*dot(k,t1))+exp(1i*dot(k,t2)));
  m(3,2)=conj(m(2,3));
  m(2,4)=HCds_Ss_principal;
  m(4,2)=HSs_Cds_principal;
  M(1,3)=HCdpz_Spz_principal;
  M(3,1)=HSpz_Cdpz_principal;
  M(2,3)=HCdpz_Spz*(1+exp(1i*dot(k,t1))+exp(1i*dot(k,t2)));
  M(3,2)=conj(M(2,3));
  M(2,4)=HCdpz_Spz_principal;
  M(4,2)=HSpz_Cdpz_principal;
end
hold off

%IMPLIMENTATION OF EQUATION A.3

[v d]=eig(m);
[V D]=eig(M);

%PLOT OF ENERGY STATES IN K2 DIRECTION

plot([0 50],[d(1,1) d(1,1)],'r-',[0 50],[D(1,1) D(1,1)],'c-');
plot([0 50],[d(3,3) d(3,3)],'b-',[0 50],[D(3,3) D(3,3)],'m-');

%PLOT OF ENERGY OF DISPERSION BAND FOR THE SECOND BAND IN K2 DIRECTION

kk=sqrt(dot(k,k));
if kk==0
  sign=-1;
end
plot(sign*kk,d(3,3),'b:o');%**NOTE THE ENERGY STATES PLOT IS REMOVED OR COMMENTED OUT WHEN PLOTTING THE BAND**
C.2 Microring Switch

```matlab
hold on;
t = 0.95;
n_eff = 1.6;
n_dots = 1.8*(10^-12);%cm^2/W
L_ring = 1500; % in nanometers
I_ring = 0;
lambda = linspace(450,650,200); % wavelength in nanometers
theta = ((2*pi*L_ring*n_eff)+(2*pi*n_dots*I_ring*L_ring))./lambda;
power2 = (2*t^2)*(1-cos(theta));
power = 1+ (t^4)-(2*t^2)*cos(theta);
y = power2./power;
plot(lambda,y,'k');
I_ring = 30000*(10^6); % W/cm^2
theta = ((2*pi*L_ring*n_eff)+(2*pi*n_dots*I_ring*L_ring))./lambda;
power2 = (2*t^2)*(1-cos(theta));
power = 1+ (t^4)-(2*t^2)*cos(theta);
y = power2./power;
plot(lambda,y,'k:.');
xlabel('wavelength (nm)')
ylabel('Transmission coefficient')
hold off;
```

C.3 Fabry Perot

```matlab
Reflection
r = 0.3;
delta = linspace(-2*pi,4*pi,50);
finesse = (2*r/(1-r^2))^2;
b = 1+((finesse*(sin(delta./2)).^2)/b);
y = ((finesse*(sin(delta./2)).^2)./b);
hold on;
r = 0.2;
delta = linspace(-2*pi,4*pi,50);
finesse = (2*r/(1-r^2))^2;
b = 1+((finesse*(sin(delta./2)).^2)/b);
y = ((finesse*(sin(delta./2)).^2)./b);
hold on;
r = 0.1;
delta = linspace(-2*pi,4*pi,50);
finesse = (2*r/(1-r^2))^2;
b = 1+((finesse*(sin(delta./2)).^2)/b);
y = ((finesse*(sin(delta./2)).^2)./b);
hold on;
r = 0.7;
delta = linspace(-2*pi,4*pi,50);
finesse = (2*r/(1-r^2))^2;
b = 1+((finesse*(sin(delta./2)).^2)/b);
y = ((finesse*(sin(delta./2)).^2)./b);
hold on;
r = 0.8;
delta = linspace(-2*pi,4*pi,50);
finesse = (2*r/(1-r^2))^2;
b = 1+((finesse*(sin(delta./2)).^2)/b);
y = ((finesse*(sin(delta./2)).^2)./b);
hold on;
```
\( r = 0.93; \)
\[
\text{delta} = \text{linspace}\left(-2\pi, 4\pi, 50\right);
\]
\[
\text{finesse} = \left(\frac{2*r}{(1-r^2)}\right)^2;
\]
\[
b = 1 + \left(\text{finesse} \times \left(\sin(\text{delta}/2)\right)^2\right);
\]
\[
y = \frac{1}{b};
\]
\[
\text{plot}\left(\text{delta}, y, 'g'\right);
\]
\[
\text{xlabel('phase')}
\]
\[
\text{ylabel('Reflection coefficient')}
\]

Transmission

\( r = 1; \)
\[
\text{delta} = \text{linspace}\left(-2\pi, 4\pi, 50\right);
\]
\[
\text{finesse} = \left(\frac{2*r}{(1-r^2)}\right)^2;
\]
\[
b = 1 + \left(\text{finesse} \times \left(\sin(\text{delta}/2)\right)^2\right);
\]
\[
y = \frac{1}{b};
\]
\[
\text{plot}\left(\text{delta}, y, 'k'\right);
\]
\[
\text{hold on;}
\]
\( r = 2; \)
\[
\text{delta} = \text{linspace}\left(-2\pi, 4\pi, 50\right);
\]
\[
\text{finesse} = \left(\frac{2*r}{(1-r^2)}\right)^2;
\]
\[
b = 1 + \left(\text{finesse} \times \left(\sin(\text{delta}/2)\right)^2\right);
\]
\[
y = \frac{1}{b};
\]
\[
\text{plot}\left(\text{delta}, y, 'm'\right);
\]
\( r = 3; \)
\[
\text{delta} = \text{linspace}\left(-2\pi, 4\pi, 50\right);
\]
\[
\text{finesse} = \left(\frac{2*r}{(1-r^2)}\right)^2;
\]
\[
b = 1 + \left(\text{finesse} \times \left(\sin(\text{delta}/2)\right)^2\right);
\]
\[
y = \frac{1}{b};
\]
\[
\text{plot}\left(\text{delta}, y, 'c'\right);
\]
\( r = 0.7; \)
\[
\text{delta} = \text{linspace}\left(-2\pi, 4\pi, 50\right);
\]
\[
\text{finesse} = \left(\frac{2*r}{(1-r^2)}\right)^2;
\]
\[
b = 1 + \left(\text{finesse} \times \left(\sin(\text{delta}/2)\right)^2\right);
\]
\[
y = \frac{1}{b};
\]
\[
\text{plot}\left(\text{delta}, y, 'b'\right);
\]
\( r = 0.8; \)
\[
\text{delta} = \text{linspace}\left(-2\pi, 4\pi, 50\right);
\]
\[
\text{finesse} = \left(\frac{2*r}{(1-r^2)}\right)^2;
\]
\[
b = 1 + \left(\text{finesse} \times \left(\sin(\text{delta}/2)\right)^2\right);
\]
\[
y = \frac{1}{b};
\]
\[
\text{plot}\left(\text{delta}, y, 'r'\right);
\]
\( r = 0.93; \)
\[
\text{delta} = \text{linspace}\left(-2\pi, 4\pi, 50\right);
\]
\[
\text{finesse} = \left(\frac{2*r}{(1-r^2)}\right)^2;
\]
\[
b = 1 + \left(\text{finesse} \times \left(\sin(\text{delta}/2)\right)^2\right);
\]
\[
y = \frac{1}{b};
\]
\[
\text{plot}\left(\text{delta}, y, 'g'\right);
\]
\[
\text{xlabel('phase')}
\]
\[
\text{ylabel('Transmission coefficient')}
\]


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