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A PHOTOLUMINESCENCE SCALING STUDY OF CdSe/ZnSe SELF ASSEMBLED QUANTUM DOTS

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DOTS

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Abstract

A scaling study was conducted to determine the optical properties of CdSe/ZnSe self-assembled quantum dots (SAQD) as a function of changing aperture area. To accomplish this, photoluminescence (PL) experiments were performed on a sample consisting of a (100) GaAs substrate, a 1 µm ZnSe buffer layer, ~3 monolayers of CdSe (forming the SAQD), and a 50 nm ZnSe capping layer through 16 apertures ranging in area from ~21.76 through 0.006 µm².

The PL spectra from the CdSe SAQD are composed of sharp peaks seemingly dispersed on a broad feature. Two models that explain these spectral features are a single and a multiple energy state model. The multiple energy state model assumes that both the sharp peaks and the broad feature are real, distinct characteristics of the quantum dot energy landscape, while the single energy state model assumes that the broad feature is an artifact from the overlap of the individual sharp peaks. To test this the broad and the sharp features from PL spectra were isolated and the fractional integrated intensity of the features were determined for each of the aperture areas. The ratio of the sharp/broad fractional integrated intensity was then plotted as a function of changing aperture area. If the single energy state model were correct, the broad feature would vanish with a significant reduction in aperture area. This is not the case; the area of the broad feature persists for even the smallest of aperture areas.
To further test the two models, several simple simulations were performed. These simulations generate a distribution of individual sharp peaks and plot their superposition. The sharp/broad fractional integrated intensity for these simulated spectra was then plotted and compared to the results from the experimental PL spectra. None of the simulation results reproduce the experimental results. When two of the simulated spectra were added together (simulating the multiple energy state model), the sharp/broad fractional integrated intensity is very similar to the experimental results. This suggests that the multiple energy state model describes the PL spectra and the CdSe SAQD energy landscape while the single energy state model does not.
Like myself,

this thesis is dedicated

to Donna, Christian, Angela & Carl;

my loving wife and children.
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Chapter 1
Introduction

1.1 Objectives

The advent of sophisticated micro- and nano-fabrication techniques allows for the unique opportunity for studying particle confinement in one, two, and three dimensions. Aside from this being a fascinating subject from the standpoint of fundamental physics, it has application to the rapidly growing efforts in device research and development by the computer and telecommunication industries. The ability to study reduced dimensional structures started over three decades ago with the fabrication of a thin film semiconductor with a thickness on the order of the De Broglie wavelength ($\lambda = h/p$; where $h$ is Planck’s constant and $p$ is the momentum of the particle) sandwiched between two semiconductors with larger band gaps. Such a structure is referred to as a quantum well due to the one-dimensional confinement perpendicular to the plane of the thin film. From this beginning, thin films were further confined in an additional direction creating quantum wires and these wires were further confined to produce quantum boxes, referred to as quantum dots.

Quantum dots (QD) can be fabricated by etching away portions of thin films leaving fabricated quantum boxes. Materials for thin films can also be chosen such that QD will self assemble. One way Self Assembled Quantum Dots (SAQD) arise is from a lattice mismatch that causes strain between the substrate and the thin film, which has a thickness on the order of a few individual atomic layers, monolayers (ML). After a few ML of the
thin film are grown epitaxially, strain leads to the spontaneous formation of small domed islands or pyramid like structures called SAQD.

The aim of this work is to investigated the optical properties of CdSe/ZnSe SAQD using Photoluminescence (PL) through aperture areas ranging from ~ 21 to 0.006 µm². Comparing the experimental PL results to a model of a PL spectrum composed of overlapping discrete emissions using a Monte Carlo simulation will provide information about the CdSe/ZnSe SAQD energy landscape.

The remainder of Chapter One will introduce the concepts and properties of reduced dimensional structures, detail the properties of CdSe SAQD, and provide motivations for this research. Chapter Two develops the experimental setup necessary to conduct the PL experiment. The results of the PL experiments through apertures from ~ 21 to 0.006 µm² will be described in Chapter Three. Development and results of a Monte Carlo simulation depicting a spectrum composed of the overlap of individual sharp peaks will be introduced in Chapter Four. Chapter Five will include a comparison of the experimental PL and simulation results. An alternative model depicting two distinct energy states will also be presented and compared with the experimental PL results in Chapter Five. Lastly, Chapter Six will contain a summary of the findings of these experiments.

1.2 The effects of dimensional reduction on semiconductor properties
When the study of semiconductors moves from the bulk properties of materials, having approximately infinite extension in all directions, towards increased spatial confinement the effects predicted by quantum mechanics become increasingly important. One example is the ability to predict the effects such confinement has on the allowed electron energy states. As illustrated in Figure 1.2 a, the density of states for a bulk sample forms a continuum as a function of increased energy. The expression for the density of states, \( D(E) \), in a bulk semiconductor is given by [1]:

\[
D(E) = \left( \frac{m^*}{\hbar^2} \right)^{3/2} \left( \frac{2E}{\pi^2} \right)^{1/2}
\]

where \( m^* \) is the effective mass of the particle. When one-dimensional confinement of a particle occurs in a quantum well, Figure 1.2 b, the density of states is altered. This

**Figure 1.1:** Illustration of the effect that increased spatial confinement has on the density of states for (a) a bulk material, (b) a quantum well, (c) a quantum wire, and (d) a quantum dot. *Modified from Robinson*
produces steps in the density of states as a function of allowed energies. The expression for the density of states, \( D(E) \), in a semiconductor quantum well is given by [1]:

\[
D(E) = \left( \frac{m^*}{\hbar^2} \right) \sum_n \Theta(E - \varepsilon_n)
\]

where the discrete energy levels are given by \( \varepsilon_n \), with \( n \) summed over all possible states.

With an increase to two dimensions of spatial confinement, Figure 1.2 c, the allowed energies are further restricted. The expression for the density of states, \( D(E) \), in a semiconductor quantum wire is by [1]:

\[
D(E) = \left( \frac{2m^*}{\hbar^2 \pi^2} \right)^{1/2} \sum_{n_x,n_y} \frac{1}{\sqrt{E - \varepsilon_{n_x,n_y}}} \Theta(E - \varepsilon_{n_x,n_y})
\]

Then in Figure 1.2 d, discrete \( \delta \)-function like energy states indicate the effect of three-dimensional confinement. Thus, the expression for the density of states, \( D(E) \), in a semiconductor quantum dot is given by [1]:

\[
D(E) = 2 \sum_{n_x,n_y,n_z} \delta(E - E_{n_x,n_y,n_z})
\]

1.3 Properties of CdSe/ZnSe SAQD
The strain due to a lattice mismatch between the CdSe and the ZnSe is one possible mechanism attributing to the spontaneous formation of CdSe SAQD. The individual properties of CdSe and ZnSe are briefly reviewed below.

ZnSe has a cubic (zinc-blende) structure with a lattice site separation distance of \( a = 0.5667 \) nm. ZnSe is an II – VI material. This means it is comprised of Zn, a transition element in Group II B from the periodic table having an electron orbital structure of \([\text{Ar}]4s^23d^{10}\) and Se, in Group VI A, having an electron orbital structure of \([\text{Ar}]4s^23d^{10}4p^4\).

CdSe normally crystallizes into a hexagonal (wurtzite) lattice but when it is grown epitaxially, atom-by-atom, on a cubic buffer layer it assumes the cubic lattice structure. The lattice spacing distance for CdSe which crystallizes in the cubic formation is \( a=0.6050 \) nm and it is also a II – VI material. The electron orbital structure for Cd is, \([\text{Kr}]\ 5s^24d^{10}\), were the larger Kr core in Cd accounts for the larger lattice spacing than ZnSe.

Thus, at the interface between a ZnSe and a CdSe layer there is an \( \sim 7\% \) lattice mismatch due to the difference in the lattice spacing. This mismatch results in strain that contributes to the formation of domed island-like CdSe structures.

### 1.4 Motivations for the PL study of CdSe SAQD through decreasing aperture size.

The topic of CdSe/ZnSe SAQD has proven to be a fascinating area of research with many of unanswered questions. The purpose of this section is to present some of those
questions and address some of the topics that directly influenced the choice and direction of this research.

In order to control the growth of CdSe SAQD, which is essential for making and improving devices, more information needs to be compiled concerning how the QD form and how they behave electrically and optically. In-situ reflective high energy electron diffraction (RHEED) patterns provide evidence for CdSe QD formation [2]. The transformation from 2D, represented by a streaky 2 x 1 reconstruction, to a spotty pattern after deposition of 2.5 to 3.0 ML of material is an indicator of 3D QD formation. The presence of QD during the growth process is supported by micro-photoluminescence on CdSe samples capped with a transparent layer of ZnSe after 0.5 to 2.6 ML of CdSe growth. The micro-photoluminescence study reports sharp response lines with typical widths of 200 $\mu$eV superimposed on a broad luminescence [2]. The broad luminescence shifts to lower energies (~ 2.77 to 2.33 eV) with an increase in CdSe thickness from 0.5 to 2.6 ML. Sharp lines were observed on all CdSe thicknesses indicating QD, although the quantity was much diminished at the 0.5 ML thickness. The presence and growth characteristics are further explored using a scanning transmission electron microscope (STEM) [2]. This method, combined with the PL study, suggest a platelet growth as a precursor to QD formation rather than the formation of the typical wetting layer found in other self assembled quantum dot materials [2].

Cathodoluminescence and photoluminescence studies have also been conducted in an attempt to better understand the growth mechanism of CdSe SAQD. These studies have suggested the presence of two simultaneous growth modes leading to the formation of two distinct types of QD [3]. This process produces QD less than 10 nm in diameter and
QD greater than 16 nm in diameter. Atomic Force Microscopy (AFM) and RHEED have also been used to determine CdSe QD densities. These have been reported as $2 \times 10^9 \, \text{cm}^{-2}$ ($20 \, \mu\text{m}^{-2}$) [4] by ex-situ tapping mode AFM, $5 \times 10^{11} \, \text{cm}^{-2}$ ($5 \times 10^3 \, \mu\text{m}^{-2}$) by [5], $6 \times 10^{10} \, \text{cm}^{-2}$ ($600 \, \mu\text{m}^{-2}$) [6], and an in-situ UHV-AFM measurement of $7 \times 10^{10} \, \text{cm}^{-2}$ ($700 \, \mu\text{m}^{-2}$) [7]. Due to the in-situ nature of the UHV-AFM study, a QD density of $700 \, \mu\text{m}^{-2}$ will be assumed from this point on.

Additionally, properties pertaining to the existence of two unique energy states associated with individual QD by PL experiments have been reported. In a temperature dependence study Kim et al. [8] reported sharp lines with full width at half maximum (FWHM) of $\sim 200 \, \mu\text{eV}$ present at low temperatures ($T \approx 5 \, \text{K}$) being replaced by features with FWHM of $3 – 5 \, \text{meV}$ ($T \approx 70 \, \text{K}$). Additional in-situ UHV-AFM measure CdSe SAQD to be approximately $1.5 – 3.5 \, \text{nm}$ in diameter an average height $\sim 2.3 \, \text{nm}$ [7]. The PL spectra from CdSe SAQD is reported to be composed of sharp peaks measuring $150 – 400 \, \mu\text{eV}$ superimposed on a broad feature measuring $\sim 60 \, \text{meV}$. This study confirmed the sharp peaks disappearing at $\sim 70 \, \text{K}$ and prominent $3 – 5 \, \text{meV}$ features persisting until $300 \, \text{K}$. From these results Kim et al. [8] calculated the activation energies to be $4.0 \pm 0.6 \, \text{meV}$ for the sharp features and $42 \pm 7 \, \text{meV}$ for the broad features with line widths greater than $3 \, \text{meV}$. In a time resolved PL experiment Robinson et al. [9] reported recombination life times of $4 \, \text{ns}$ for the sharp lines and $450 \, \text{to} \, 700 \, \text{ps}$ for the spectral line widths greater than $3 \, \text{meV}$. All of these studies support the existence of two distinct and unique energy states. Determining if there is one energy state or two distinct energy states is the focus of this research. The motivation for the work in this thesis is that spectra for these two cases should exhibit strikingly different behaviors as a function of
the number of quantum dots sampled. In one case (only a single energy state), the broad background should disappear entirely as the number of dots is reduced, while in the other case (two energy states) the relative fraction of PL intensity from the sharp peaks and the broad background should be approximately stable as the number of dots is reduced. PL obtained from CdSe SAQD samples through a series of apertures decreasing in size will allow for the comparison of sharp and broad spectral features and determine if scaling exists. The sharp and broad features are features of the CdSe SAQD PL spectra and will be discussed in Chapter 2. Also, a comparison of the experimental PL results to several simple simulations of the spectral overlap of individual (one energy state) and multiple (two energy states) sharp peaks will provide information about which model better describes the energy landscape of the QD sample.
Chapter 2
Experimental Aspects

The purpose of this chapter is to introduce elements and methods necessary to understand and conduct this experiment. It will include a brief description about the growth of the CdSe/ZnSe SAQD sample, a description of photoluminescence (PL) theory and the setup used in the PL experiment. The section on PL also includes a preliminary power dependence study and a temperature dependence study. These were conducted to optimize parameters before conducting the PL experiment through the apertures. Also in this chapter is a description of the fabrication techniques used to form the apertures and Atomic Force Microscopy (AFM) used to characterize the apertures.

2.1 CdSe SAQD fabrication

The quantum dot sample used throughout these experiments (shown in Figure 2.1) was prepared by first depositing a 1µm thick ZnSe buffer layer on a (100) GaAs substrate. Approximately three monolayers (ML) of CdSe were then grown onto the ZnSe forming the SAQD. This was capped with 50 nm of ZnSe to prevent evolution of the GaAs substrate.

Figure 2.1: Vertically exaggerated illustration of the CdSe self assembled quantum dot sample used in the PL experiments. The sample was grown by MBE and consist of a (100) GaAs substrate, a 1μm buffer layer of ZnSe, ~3ML of CdSe (forming the SAQD), and 50 nm of ZnSe capping layer.
quantum dots. The sample was grown in a Riber 32 R&D molecular beam epitaxy (MBE) machine with a growth rate of ~14 seconds per ML at 300 C. One method used to confirm the presence of quantum dot growth is reflective high-energy electron diffraction (RHEED). A transition from streaky, implying two-dimensional growth, to spotty in the RHEED pattern provides evidence for the growth of localized three-dimensional quantum dots [2]. For additional methods confirming the presence of SAQD see Section 1.4.

2.2 Photoluminescence

One powerful tool for studying the exciton properties of reduced dimensional structures is Photoluminescence (PL). In a constant wave (CW) PL experiment, the number of photons emitted during electron-hole recombination is measured as a function of energy. When an electron is excited with energy greater than that of the bandgap it undergoes a transition from the valence band to the conduction band leaving behind a hole in the former. Through a variety of different processes such as phonon assisted relaxation, the electron and hole relax to the bottom of the conduction band and the top of the valance band forming a bound state (an exciton). The final annihilation of the exciton occurs when the electron and hole recombine. In this process both energy and momentum are conserved. The recombination of an electron with a hole of opposite momentum is accompanied by the emission of a photon. The characteristic energy of the photon is equal to the difference in energy between the electron and hole just prior to recombination. Spectra from band to band recombinations are often broad with a distribution of emission energies proportional to the distribution of carriers in the band.
This is due to incomplete relaxation of the electron-hole pair prior to recombination. In this experiment low temperatures of ~5 K were maintained to allow full relaxation of the exciton prior to recombination. This technique provides compositional information, information about the electric structure, and a bandgap measurement for the material.

Both CdSe and ZnSe are direct bandgap materials. This means that the top of the valence band is very closely aligned to the bottom of the conduction band in k-space (Figure 2.2). This is unlike indirect bandgap materials where the bottom of the conduction band does not align with the top of the valence band in k space. These indirect band gap materials need phonon assistance for electron-hole recombination to conserve momentum. Alignment of the direct band gap materials in k space and the low temperatures maintained during this experiment lead to narrow spectral widths due to their narrow origins in k-space. It is this property of CdSe and ZnSe that allows for direct

Figure 2.2: The processes involved in electron-hole recombination in a direct bandgap material such as CdSe and ZnSe. (a) The relaxation process from an initial excitation much greater than the bandgap energy to the bottom of the conduction band and the top of the valence band by the electron and the hole that leads to band to band recombination. (b) Exciton recombination originating from a fully relaxed, bound electron hole pair. [1]
bandgap measurements by PL and narrow, delta function like, emissions from individual QD.

In all of the experiments, a CW argon laser provided the photon excitation of 514.5 nm (3.429 eV). Figure 2.3 illustrates the design of the PL experiment: the laser is sent through a set of optics consisting of attenuating filters to control laser power levels, an iris to collimate the laser beam, and deflecting mirrors to adjust the path of the laser.

**Figure 2.3:** Illustration depicting the PL experimental configuration. The experiment (unless indicated) will be conducted with a laser power of ~85 µW, a cryostat temperature of 5 K, and the spectrometer in direct mode. [reference]
beam. The laser beam is then focused on to the sample through an Olympia microscope fitted with a 50x long working length objective. Further, the sample is kept at 5 K for all experiments (unless otherwise stated) by a Janis cold finger cryostat. After laser excitation, which creates the electron hole pairs, the emitted light (due to recombination) is collected in a backscattering configuration through a holographic filter (used to remove the scattered laser light) into the spectrometer operating in the direct mode. In direct mode, the spectrometer has an optical configuration that optimizes spectral resolution while maintaining high emission intensities. The signal was finally detected by a charge coupled device (CCD) camera and analyzed by the computer software (LabSpec).

Before conducting PL experiments, the spectrometer needs to be calibrated. To do this the 2.42 eV line ($\lambda = 514.5$ nm) produced from the argon laser and the 2.345 eV Ramen line ($k = 521.5$ cm$^{-1}$) from a Si sample are used. These sharp stable spectral peaks can be compared to the calibration of the spectrometer until agreement is achieved. The calibration spectra used in this experiment are presented in Figure 2.4.

![Figure 2.4: Spectra used to calibrate the spectrometer. (a) Argon laser spectrum with a peak at $E = 2.42$ eV, $\lambda = 514.5$ nm. (b) Si spectrum with a peak at $E = 2.345$ eV, $k = 521.6$ cm$^{-1}$]
2.2.1 Power dependence

Laser excitation with too much power has been shown to alter the energy landscape of a quantum dot sample. In fact, using excessive power can lead to a permanent shift in quantum dot PL spectral features. This would destroy any reproducibility in the experiment and needs to be avoided. To avoid this pitfall, individual emission peaks from CdSe SAQD were studied as a function of increased power (Figure 2.5). By evaluating the change in intensity for individual peaks (associated with PL from individual QD) as a function of increased laser power, an optimum power level for conducting the experiment was determined. In the same configuration as Figure 2.3 and starting with a laser power of 63 μW, as measured before the optics, the laser power was increased consistently by a factor of two until a power of three mW was reached. Measuring the laser power directly above the cryostat window indicates an order of magnitude drop in the laser power due to the optics. Thus, this study ranges from approximately 6.5 to 300 μW at the sample. After the spectrum was taken at 3 mW, the laser power was reduced and additional PL spectra were taken. These additional spectra were very different from the original spectra in individual peak locations. This indicates that the quantum dot energy

![Figure 2.5: Intensity vs. Laser power for PL spectra](image-url)
landscape is permanently altered at laser power levels greater than ~ 1.5 mW. Figure 2.5 also indicate that the optimum power setting for conducting the PL experiments occurs at approximately 850 µW. This point is the highest power level in the curves that are still in a linear regime. Thus, the laser power is at a maximum safe level for the sample.

2.2.2 Temperature dependence

In addition to variations in laser power, variations in temperature can also have a pronounced effect on the QD PL spectra. The discussion about electron-hole recombination in Section 2.1 alluded that higher temperatures lead to the population of higher energy states or recombination taking place prior to complete relaxation. The temperature dependence of CdSe SAQD was studied using a CW argon ion laser at a wavelength of 514.5 nm in accordance to the configuration of Figure 2.3. Starting at ~5.4 K the temperature of the cryostat cold finger was increased in ~ 5 K increments. Figure 2.6a indicates that increasing the temperature decreases the intensity of the sharp peaks while the intensity of the broad spectrum remains virtually unaffected. Similar studies have suggested that the decrease in the intensity of the sharp peaks continue until they completely disappear at ~ 70 K. This temperature also marks the appearance of lumpy features with FWHM between 3 – 5 meV that may have the same origins as the broad PL. This study suggests that the increased thermal energy excites confined electrons into higher energy states. This population of a higher energy state would account for the broader spectral PL features. In addition there is a shift in the position of the sharp peaks to lower energies with increased temperature (Figure 2.6 b). Similar results have been reported in previous experiments [8]. The differences in temperature
dependence for the sharp peaks and lumpy features, further suggest that the sharp peaks are distinct from the broad features and thus, the two are independent. The importance of this result will become apparent in Chapter 4 and 5 when they will be incorporated in the parameters of a Monte Carlo simulation.

![Figure 2.6](image)

**Figure 2.6:** (a) Temperature dependence for CdSe SAQD PL spectra. (b) Temperature dependence for a single quantum dot. The spectra in the plots are vertically shifted.

### 2.3 Aperture fabrication methods

Two methods of aperture fabrication on the CdSe/ZnSe sample surface were investigated to facilitate micro and nano PL. These methods are electron beam lithography and polysphere fabricated apertures. Although, electron-beam lithography was employed to fabricate the apertures that were used during the course of this
experiment, the polysphere fabrication method is an ongoing area of development and worth mentioning.

2.3.1 Electron-beam lithography

Electron-beam lithography provides for a precise, if complicated, method for fabricating nanoscale features (apertures) limited in size only by the final focus of the electron beam and the material properties of the resist. This method can be accomplished by equipping a scanning electron microscope with a computer controlled writing accessory that controls the rastering of the beam. Following the series of steps presented in Figure 2.7 apertures as small as 40 nm² have been fabricated. For additional information about the processing steps and similar techniques see Turck et al. [10]
Figure 2.7: illustration depicting the electron beam lithography process used to fabricate apertures. The process steps are: (1) the sample is cleaned and prepped with an agent to promote adhesion of the resist. (2) A layer of resist is then uniformly spun onto the sample surface. (3) Resist is then exposed to the electron beam, writing the desired aperture size and shape directly on the resist surface. (4) A chemical bath is used to remove (develop) the resist not exposed. (5) An aluminum film is evaporated onto the sample surface with a thickness less than that of the resist thickness. (6) The remaining resist and the aluminum that covers it, are removed by the technique of lift off in an ultrasound chemical bath.
2.3.2 Polysphere aperture fabrication technique

Electron beam lithography is a proven method for fabricating micro- and nano- apertures. Unfortunately the specialized equipment necessary for e-beam lithography is not always available and often the loss of time and money associated with having the work done elsewhere is unacceptable. This has been the motivation for the development of a polysphere aperture fabrication method. In this method, latex spheres are used to block the deposition of metal. These blocked areas form apertures once the spheres are removed. Difficulties such as clumping of the spheres due to surface tension, chemical break down of the spheres due to solvent interactions, and an inadequate means of measuring aluminum film thickness during deposition made fabricating apertures by this method challenging. In the end, promising initial success in developing an inexpensive and reliable means of fabricating multiple apertures of uniform and controllable size has been achieved. This section will describe the process used to avoid sphere clumping by diluting the number of spheres present in the mixture and adding ethyl glycol. It will then detail the fabrication process and demonstrate the fabrication results.

The first challenge in developing this method was to overcome the problems of spheres clumping together and to deposit a desired density of spheres onto the sample surface. Clumping of the spheres (Figure 2.8) has been observed in two forms:

1) The surface tension in the drop of liquid pulls the sphere in toward the center as the volume of the drop decreases due to evaporation. This leads to a high concentration of spheres at the edge of a ring when the drop dries (Figure 2.8a).
2) Spheres tend to be found in groups. Presumably this is due to a static attraction. Thus once two spheres collide they are stuck. Ethyl glycol is added to help prevent this type of clumping due to its viscous nature (Figure 2.8b).

![Figure 2.8: SEM images of gold coated 950 nm spheres (a) The effects of extreme clumping around the edges (b) The effect of clumping towards the center due to spheres getting stuck together.](image)

Initially spheres are packaged in distilled deionized water with a concentration given in percent solid. For example, the 950 nm diameter spheres are 2.5 % solid per volume.

The goal for a desired concentration is to have approximately one aperture per 5 µm area. To accomplish this, the percent solid must be converted into number of spheres per volume. Through out the development of this process as well as during the experiments, small volumes of liquid mixtures will be distributed from a Fisher 5 ¾ inch pipette. These pipettes deliver 0.03 mL of water per drop. To calculate the number of spheres per drop, it will be assumed that the drops as well as the latex spheres are perfect spheres with a volume of \( \frac{4\pi r^3}{3} \). The first dilution (Mixture #1) included 35 mL deionized distilled water plus one drop latex sphere solution. Mixture # 1, is again diluted to form mixture #2. Mixture #2 consist of two drops mixture # 1 plus two drops ethyl glycol plus
six drops deionized distilled water. An example of the calculation yielding the number of latex spheres per drop and thus, per area, of for mixture #1 and #2 are provided in Apendix A. Table 2.1 lists the results of the calculations for 170, 356, 532, 752, and 950 nm diameter spheres. It is not yet obvious if these concentrations are optimized for sphere concentration.

<table>
<thead>
<tr>
<th>Sphere diameter (nm)</th>
<th>Sphere density (\text{per area (A = 50 \mu m}^2))</th>
</tr>
</thead>
<tbody>
<tr>
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<td>18</td>
</tr>
<tr>
<td>752</td>
<td>38</td>
</tr>
<tr>
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<tr>
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</tr>
</tbody>
</table>

**Table 2.1:** The results of calculations to determine the number of 950, 752, 532, 356, and 170 nm latex spheres found in a 50 \(\mu m}^2\) area.

To verify the sphere density in the mixture a drop of the second mixture was applied to the surface of a glass slide. The slide was then soft baked in an oven at 100 C for 5 minuets until the liquid evaporated. A Hummer DC gold sputtering device then coated the spheres, as well as the glass, with a conducting layer. This allowed for direct inspection of the sphere densities by means of a Scanning Electron Microscope (SEM). Images of the sphere densities and the clumping are illustrated in Figure 2.8a and 2.8b. These predicted sphere densities will in practice be much lower towards the center of the applied area due to sphere clumping from surface tension at the edges of the evaporating water droplet. With the desired sphere concentrations achieved, the next step is to devise a method for fabricating the apertures using these spheres. The CdSe samples range in size from three to five mm so they must be mounted onto a larger silicon wafer or glass
slide with epoxy throughout the process. With the sample mounted, a Shipley P-20 primer is first spun on to the surface. Shipley 1818 photoresist (PR) is then spun onto each sample individually to minimize edge effects. Edge effects arise due to the non-uniform distribution of PR, which results in non-uniform resist thickness across the resist. A simple photolithography mask was created with five 100 µm by 200 µm rectangular features, which, using alignment features can be aligned side by side. This mask allows for the fabrication of five separate pads (dies) each containing a different size of aperture. The first die on this mask is used to expose the PR using a Karl Suss MJB3 photolithography mask aligner with a 405 nm line. The light from the aligner exposes the resist in all of the areas in the rectangular feature. The resist in the rectangular feature is thus more susceptible to being removed in a developing solution. After the resist in the rectangular feature is removed, a drop of the dilute sphere solution is applied. Being that the diameter of the drop is much greater than the size of the rectangle, all of the clumping due to edge effects are concentrated outside the desired area, leaving behind a random distribution of spheres inside the sunken area left by the removal of the PR. The PR and the sphere mixture are then hard baked for 30 minutes at 100 C. A metal with an opaque thickness much less than the sphere radius is then thermally evaporated onto the substrate. After the deposition, the resist and the metal on top of the resist are removed using the technique of lift off. With the lift off process completed, a metal pad containing multiple apertures with a random distribution and a uniform size is left behind. This process is illustrated in Figure 2.9 and can then be repeated multiple times to fabricate pads containing apertures of different sizes.
This process was attempted using 752 nm spheres from the same concentration listed above in mixture #2. The metal chosen was aluminum, which was deposited to a thickness of 40 nm using a Leybold ESV-6 electron beam evaporator with a 8 KeV accelerating voltage. AFM images have been taken to confirm the existence and uniformity of the apertures after the lift off process. These images, Figure 2.10a and 2.10b, show that the process is successful and provides an inexpensive and straightforward method of fabricating apertures for use in a variety of applications.

**Figure 2.9:** Illustration of the process steps involved in fabrication of apertures using polyspheres

thickness of 40 nm using a Leybold ESV-6 electron beam evaporator with a 8 KeV accelerating voltage. AFM images have been taken to confirm the existence and uniformity of the apertures after the lift off process. These images, Figure 2.10a and 2.10b, show that the process is successful and provides an inexpensive and straightforward method of fabricating apertures for use in a variety of applications.
2.4 Atomic force microscopy (AFM)

A Thermo Microscope Auto Probe CP unit was used to characterize the shape, size and depth of the apertures fabricated by the electron beam lithography process. The Auto
Probe CP unit is capable of operating in both contact and non-contact modes for Atomic Force Microscopy. A Si$_3$N$_4$ cantilever tip is grown protruding from the underside of the Si$_3$N$_4$ cantilever in a single growth process. As seen in Figure 2.11, this is attached to a ceramic piezo chip, which measures and regulates the oscillating frequency of the cantilever while operated in non-contact mode. The cantilever tip is brought very close to the substrate surfaces where repulsive and attractive Van Der Wall forces are dominant for use in contact and non-contact mode scans respectively (Figure 2.12). A constant force is maintained between the cantilever tip and the surface of the substrate while small variations in the height of the sample surface are translated into movement of a HeNe laser beam, reflected off the top of the cantilever. The motion of the deflected beam is then detected by a photodetector mounted to the AMF head. The motion of the laser beam relative to the photodetector is then translated into variations in the surface topography by the software. Thus, by rastering the sample, which is held on top of a piezo-electric tube, beneath the cantilever tip and maintaining small variations in the height by means of a feed back loop between the photodetector and the piezo-electric tube, a topological image of the surface of the substrate can be obtained. The sample is adhered to a magnetic disk using double sided tape and magnetically held to the cap on top of the piezo electric tube to avoid any slipping during the rastering of the sample.

**Figure 2.11:** A illustration depicting the workings of the Auto Probe CP unit obtained from Park Scientific.
The quality of the image and the accuracy of the data produced in the scan is controlled by adjusting the scan parameters of force between the cantilever tip and the surface of the substrate, the rate at which the sample is rastered beneath the cantilever tip, and the gain which controls how fast variations in the force between the cantilever tip and the surface are adjusted to maintain a constant force. These parameters as well as the scan size have been adjusted to achieve the best image, which communicates the most accurate information.

An AFM in non-contact mode was used to characterize the apertures fabricated on top of the ZnSe capping layer. Non-contact mode was chosen to prevent pressure between the cantilever tip and the sample. It was felt that additional pressures, even in the nanoNewton range, could alter the energy landscape of the sample. The attractive Vander Walls Force, Figure 2.12, on the cantilever tip allows for scanning in the non-

![Figure 2.12](image.png)

**Figure 2.12**: Illustration of the regions of attractive and repulsive Van Der Walls force in terms of force and sample separation. *Picture courtesy of ThermoMicroscope*
contact regime where there is a tip sample separation distance. Thus, with the cantilever tip never in contact with the substrate any possibility of altering the energy landscape of the quantum dots due to applied force is eliminated.

The apertures were then carefully measured to obtain the height, width and depth. In order to avoid confusion that might arise from the scan, the feature in the scanned image was kept to approximately one quarter of the scan window. To confirm that the aperture were not obstructed the depth of the apertures, as well as the height and width, were measured (Figure 2.13), and compared with the 40 nm aluminum pad thickness predicted during the fabrication process. With the height and width measurement, the area of the
Figure 2.13: Atomic Force Microscope image of a 0.51 µm² aperture.
aperture can be calculated. The results of these calculations appear in Table 2.2. Areas for the circular apertures were calculated by averaging the height and width measurements, dividing by two to obtain the radius and using \( A = \pi r^2 \).

<table>
<thead>
<tr>
<th>Aperture</th>
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<th>Area</th>
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<td>24</td>
<td>0.221</td>
<td>14</td>
<td>3.526</td>
</tr>
</tbody>
</table>

**Table 2.2:** Aperture area measured in microns. The label “Aperture 11” corresponds to the aperture in the top right corner of the sample while the label “Aperture 44” is located at the bottom left of the sample. The first number refers to the column and the second number refers to the row considered from right to left.

These precisely characterized aperture areas provide the opportunity to conduct a PL scaling study. Knowing the exact dimensions of the CdSe surface exposed to laser excitation allows for the scaling between PL spectra to be studied. Further, knowing the aperture area and the approximate QD density of 700 \( \mu m^2 \) (see Section 1.4 for details), determines the approximate number of QD exposed to laser excitation as well. This will be expanded upon in Chapter 3.
Chapter 3.0
Experimental scaling study of CdSe SAQD

3.1 Objectives for PL scaling study

Due to the large number of quantum dots found in a given area, (~700 \( \mu \text{m}^2 \)) [7] the prospect of spectrally resolving the emissions from a single quantum dot is challenging. An argon laser, focused through a 50x microscope objective has an optimized spot size with a diameter of \( \sim 2 \mu \text{m} \) on the sample. This focused laser still samples an enormous number of quantum dots (~1400) and leads to unresolved sharp features in the PL spectra. The PL emissions in Figure 3.1 suggest that the sharp emission lines are not resolved. We can see that the spectral overlap of the individual sharp peaks hide the

![Figure 3.1: CdSe/ZnSe SAQD PL emission spectrum at a temperature of 5 K with spatial resolution of \( \sim 2 \mu \text{m}^2 \).]
detail of the energy landscape. Some of this detail can be resolved by conducting photoluminescence through micron and sub micron apertures to limit the sampling area. In this way fewer quantum dots will be sampled and the PL spectra will have less individual peak overlap. To this end, apertures fabricated on a CdSe/ZnSe sample (see Chapter 2) were used to limit the sampling area of the argon laser used in PL experiments. The variations in aperture area of over three orders of magnitude (from 21.7 to 0.006 \( \mu \text{m}^2 \)) provided the opportunity for the reduced area PL study. Thus, information can be gained about the scaling behavior of the energy landscape with reduced aperture area. This chapter details the PL experiments through the fabricated apertures as well as the technique used to analyze the spectra.

3.2 PL CdSe SAQD area study

To conduct PL on the CdSe/ZnSe SAQD sample, fabricated apertures were used to isolate a well-defined area. Sixteen apertures ranging in size from 21.7 to 0.006 \( \mu \text{m}^2 \) greatly limited the area of the laser access. The CdSe/ZnSe SAQD sample was mounted on the cold finger of a continuous flow cryostat at 5 K (cooled with liquid He) using the same experimental setup as in Figure 2.3. In order to conduct the experiment the individual apertures were located by first identifying a dark region where the incident light was absorbed by the CdSe surface. This region is located amidst a highly reflective metal surface. Maximizing the intensity of the PL spectra then insured that the aperture was centered and in focus. Each aperture was investigated in the back scattering configuration. Figure 3.2 through 3.9 represent spectra from all sixteen apertures in order
of decreasing aperture area. For ease of comparison all spectral data was averaged for 10 seconds. From these spectra, we can see several points: as the area of the apertures decreases (1) the peak intensity of the PL spectra decreases from \( \sim 110,000 \) to \( \sim 300 \), (2) the amount of overlap of individual sharp peaks decreases, and (3) the broad, underlying feature remains, even for the smallest apertures.
Figure 3.2: PL spectra from CdSe SAQD excited with the 514.5 nm argon laser line at 5 K through (a) a 21.78 $\mu$m$^2$ square aperture and (b) a 16.94 $\mu$m$^2$ circular aperture.
Figure 3.3: PL spectra from CdSe SAQD excited with the 514.5 nm argon laser line at 5 K through (a) a 3.53 µm² square aperture and (b) a 2.76 µm² circular aperture.
Figure 3.4: PL spectra from CdSe SAQD excited with the 514.5 nm argon laser line at 5K through (a) a 0.681 µm² square aperture and (b) a 0.502 µm² circular aperture.
Figure 3.5: PL spectra from CdSe SAQD excited with the 514.5 nm argon laser line at 5K through (a) a 0.221 \( \mu \)m\(^2\) square aperture and (b) a 0.196 \( \mu \)m\(^2\) circular aperture.
Figure 3.6: PL spectra from CdSe SAQD excited with the 514.5 nm argon laser line at 5K through (a) a 0.062µm² square aperture and (b) a 0.039µm² circular aperture.
Figure 3.7: PL spectra from CdSe SAQD excited with the 514.5 nm argon laser line at 5K through (a) a 0.067µm² square aperture and (b) a 0.034µm² circular aperture.
Figure 3.8: PL spectra from CdSe SAQD excited with the 514.5 nm argon laser line at 5K through (a) a 0.014\,\mu m^2 square aperture and (b) a 0.017\,\mu m^2 circular aperture.
Figure 3.9: PL spectra from CdSe SAQD excited with the 514.5 nm argon laser line at 5K through (a) a 0.013μm² square aperture and (b) a 0.006μm² circular aperture.
PL data through the largest aperture (Figure 3.2 a) showed little difference from the PL taken from the CdSe/ZnSe surface without apertures (Figure 3.1). The reason for this is that the laser beam is focused to a smaller diameter (~ 2 µm) than the aperture. This is no longer the case for Figure 3.3 b through 3.9 where the aperture area is 2.76 µm² and less.

An interesting feature of the PL spectra is the multitude of sharp peaks seemingly dispersed on top of a broad spectral feature. Two of the possible models that explain these spectra are a single discrete energy state model and a multiple energy state model associated with the QD energy landscape.

As the title implies, the single discrete energy state model calls for a discrete energy state associated with single delta-function like QD energy potentials. The PL spectra from the CdSe/ZnSe SAQD are composed of a multitude of discrete sharp peaks, each having a similar width and intensity. Several reasons for variations in the intensity and width can be attributed to small variations in local stresses, QD size, or composition [8]. In this model, the difference in energy between the sharp peaks is much less than the individual sharp peak width. This leads to individual sharp peak overlap referred to as spectral overlap. The superposition of the overlap from ~ 700 µm⁻² of these sharp peaks constructs the broad feature. Thus, in this model the broad feature does not exist as a real phenomenon, rather the PL from the CdSe/ZnSe energy landscape is composed of the superposition of many sharp peaks. The single discrete energy state model will be further examined in Chapter 4.
In the multiple energy state model, at least two energy states exist in each QD. A possible model for such a potential is presented in Figure 3.10. In this model, the edges of the QD would have a delta-function like potential while the interior of the QD would have an energy band structure similar to a quantum well. These energy states would produce a PL emissions spectrum that included a sharp peak and a broad peak, each distinct and unique.

If a single energy state is responsible for the CdSe/ZnSe SAQD PL spectra, one would expect that PL through apertures decreasing in area from 21.7 to 0.006 \( \mu \text{m}^2 \) would lead to a reduction in the broad feature. At some point, when the aperture area is sufficiently small, sharp peak overlap should cease to be an issue. Thus, if the single energy state

Figure 3.10: Diagram of the multiple energy state model of possible energy states available in a quantum dot. [Reference]
model were true, the broad feature should completely disappear for PL through sufficiently small apertures. From an inspection of the spectra (Figures 3.2 through 3.9), this is not the case. The broad feature persists to the smallest apertures. This suggests that both the sharp and broad features are unique real features.

3.3 Analysis of experimental PL data

Several questions of interest arise through a visual inspection of Figures 3.2 through 3.9. Namely, (1) How do the sharp peaks scale relative to the broad feature while reducing the aperture area? and (2) How do the individual peaks change while reducing the aperture area? This section will establish a method for isolating the individual sharp peaks and defining the broad feature, present the results of comparing the fractional area of the sharp peaks and the broad feature, and an analysis of how individual sharp peaks change with a change in aperture area.

3.3.1 Method for determining the sharp/broad response

This section will examine how the sharp and broad features present in the PL spectra (Figures 3.3 through 3.9) change in response to the reduction in aperture area. To make this comparison, the ratio of the sharp divided by the broad fractional integrated intensity (the area associated with each spectral feature) was plotted as a function of aperture area. The method used to calculate this consist of the following steps: (1) The total integrated
intensity for the spectrum was calculated (2) the sharp features were isolated with a smooth fit to the baseline (details for this baseline fit are provided later), (3) the baseline was subtracted from the total spectrum leaving only the sharp peaks, (4) the fractional integrated intensity of the sharp peaks was calculated, and (5) the fractional integrated intensity from the sharp peaks was subtracted from the total spectral area to obtain the area associated with the broad feature. Plotting the intensity of the sharp peaks divided by the intensity of the broad feature for all the spectra provides information about how both scale with a decrease in aperture area.

A source of difficulty with this approach is how to fit a smooth baseline to the spectral data. To do this, a program was written in Mathematica and is included in Appendix B. The program takes the data from a spectrum and segments it into approximately 100 bins. The ordered pairs in each bin are sorted in order of increasing intensity so that the lowest twenty percent of these values can be isolated at the beginning of the list. These lowest values represent the relative minima in each bin. Averaging the relative minima in each bin creates a single ordered pair for each bin. These values are then plotted and fit by a Gaussian normal distribution. This distribution is of the form $A e^{-\sigma^2}$, with $0 < A < (\text{the maximum intensity value} + 2)$ and $250 < \sigma < 5000$. Starting values for these parameters are $A = (\text{the maximum intensity value})$ and $\sigma = 1000$. This method creates reproducible baselines that are consistent and make sense.

To illustrate this method, the PL spectrum through a 0.039 $\mu$m$^2$ aperture is shown in Figure 3.11a, b, and c. Figure 3.11a shows the original spectrum in red and the smooth baseline fit in blue. The process of subtracting the baseline from the total spectrum and the resulting sharp peak spectrum is illustrated in Figure 3.11b. To provide a perspective
of the areas associated with both the sharp peak spectrum and the broad feature spectrum, Figure 3.11c provides the visualization of both features at once with the area of the sharp peaks shaded in red and the area from the broad feature shaded in blue.
Figure 3.11: The above figures are the PL spectrum gathered through a 0.039 µm² aperture. They demonstrate the technique for determining fractional integrated area of the sharp peaks and the broad feature: (a) a smooth Gaussian distribution is generated to fit a baseline (b) subtracting the baseline allows for the extraction of the fractional area due to the sharp peaks. Subtracting the fractional area due to the sharp peaks from the total area allows the area of the broad feature to be calculated. (c) Representing the area due to the sharp peaks in red and the area due to the broad feature in blue allows for a visual comparison of the ratio of the two.
3.3.2 Sharp/broad fractional integrated intensity results

Plotting the ratio of the fractional integrated intensity of the sharp peaks divided by the fractional integrated intensity of the broad feature as a function of aperture area indicates how the sharp and broad features change with a reduction aperture area. Figure 3.12 shows a log-log plot of the data calculated from the experimental PL spectra (Figures 3.2 through 3.9) for apertures with areas from 21.78 to 0.006 µm². The result indicates that the area of the broad feature is approximately an order of magnitude larger than the sharp

![Log-log plot](image)

Figure 3.12: Log-log comparison of sharp peak/broad feature fractional integrated intensity as a function of decreasing aperture area.
features for the three largest apertures. This effect is associated with the apertures being larger than the focused laser (21.78, 16.94, 3.53 µm² ≥ (~2 µm)²). Both the sharp peaks and the broad feature have fractional integrated areas that are approximately equal for aperture smaller than the laser beam. Surprisingly, the difference in relative integrated intensity for the sharp/broad features differs by less than an order of magnitude. This is surprising since the area of the apertures decreases by over three orders of magnitude. This can not be explained by a single energy state model that predicts the disappearance of the broad feature for small aperture areas. On the contrary, Figure 3.12 indicates that both the sharp and the broad features scale similarly with a reduction in aperture area.

3.3.3 Scaling of Individual peak areas

Another way of analyzing the PL spectra from figures 3.3 through 3.9 is to examine how the individual peaks change with a change in aperture area. The spectra have isolated individual peaks at the high energy (2.28 – 2.32 eV) or low energy (2.16 – 2.2 eV) regions of the CdSe/ZnSe SAQD PL spectrum. Individual sharp peaks in these regions are attributed to the emissions from single quantum dots due to the lack of overlap between the peaks. By analyzing changes in the intensity, full width at half maximum, and area of these individual sharp peaks they can be studied as a function of decreasing aperture size. For this purpose, well-defined sharp peaks from both the high and the low energy extremes of the PL spectrum were chosen. A typical peak and base line is presented in Figure 3.13. This peak has a FWHM of 307 µeV and a mean energy of 2.1689 eV. The integration to determine the area under each peak was taken relative
to a baseline defined by a pair of points to the left and right of the sharp peak. All of the semi-log plots in Figure 3.14 a, b, and c, demonstrate that the values for the full width at half maximum, intensity, and area as a function of decreasing aperture area are relatively constant. The values for the FWHM in Figure 3.14 a range from ~150 to ~450 µeV with a single point with a value of over 1000 µeV. This peak is almost certainly constructed from the overlap of multiple peaks. The mean value for the FWHM is ~ 300 µeV.

Figure 3.14 b is a semi-log plot of the single sharp peak intensity as a function of aperture area. Values for the sharp peak intensity range from ~50 to ~250 measured in arbitrary

Figure 3.13: Individual peak from PL spectrum taken through a 0.017 µm² aperture for an accumulation time of 1 second.
units. The slope of this line is close to unity with a mean value of ~120. The integrated intensity of the individual sharp peaks is shown in Figure 3.14 c. These results are to be expected from similar individual quantum dots. Individual QD with approximately equal size, stress, and composition should have very similar spectra regardless of the aperture area. This is reflected in the approximately horizontal slopes in figures 3.14a, b, and c reflecting that the spectra from individual peaks are independent of aperture area. The uniform behavior of individual sharp peaks will be further developed in Chapters 4 and 5 where they will be used as simulation parameters.
Figure 3.14: Individual peak data. (a) Measured full width at half maximum measured for individual sharp peaks and plotted with respect to increasing aperture area. (b) Measured individual peak intensity plotted with respect to increasing aperture area. (c) Measured individual peak area plotted with respect to increasing aperture area.

3.4 Summary of results

PL experiments were performed through aperture areas spanning over three orders of
magnitude. From the PL spectra, studies were done on the scaling properties of the sharp and broad features as well as individual peak dynamics with respect to changing aperture size.

Changes in the broad features and sharp peak features from CdSe/ZnSe SAQD PL spectra were studied relative to variations in apertures size. From Figures 3.2 through 3.9 we can see several points as the area of the apertures decreases (1) the peak intensity of the PL spectra decreases, (2) the amount of overlap of individual sharp peaks decreases, and (3) the broad, underlying feature remains, even for the smallest apertures. By calculating the fractional integrated intensity associated with the broad and sharp features a ratio of sharp/broad could be calculated. When these results are plotted verses changes in aperture area (Figure 3.12), they showed that both the sharp peaks and the broad features have fractional integrated intensities that are approximately equal for aperture smaller than the laser beam size.

The study of individual peak dynamics as a function of decreasing sampling area has shown that very little difference exists between individual peaks sampled through a 21.783 µm² aperture and a 0.006 µm² aperture. One explanation for this result is a small variation in attributes from one quantum dot to another across the sample. Similarity among the QD can be explained by recalling that immediately after growth, a 50 nm transparent ZnSe capping layer was deposited on the CdSe SAQD sample. This prevents QD evolution from causing degeneration in the long-range uniformity of the quantum dots. The significance of individual peak similarities will be utilized in Chapters 4 and 5 by providing information used as simulation parameters for QD PL.
These two studies suggest several interesting conclusions (1) the individual peaks can be isolated and attributed to the emissions from a single QD due to the lack of peak overlap, (2) PL from individual QD is unaffected by variations in aperture area, (3) the broad feature does not disappear, even for PL though the 0.006 µm² aperture, and (4) a single energy state model may not be satisfactory in explaining the PL spectra since the broad feature does not disappear.
Chapter 4
Monte Carlo Simulation of SAQD scaling properties

4.1 Objectives

To further explore how the PL spectra from CdSe/ZnSe SAQD scale with a reduction in aperture area, we want to test how individual peaks would behave when superimposed in a simulation of a PL spectrum. This is simulating the single energy state model to explaining the spectra emitted by CdSe/ZnSe SAQD. Recall, that the single energy state model requires the entire PL spectrum to be composed of individual sharp peaks. The overlap of these sharp peaks is responsible for producing the entire CdSe/ZnSe PL spectrum. That is, any appearance of a broad feature in the spectrum is attributed to the superposition of the individual sharp peaks; the broad feature is not a real or distinct feature. Thus, the sharp peaks would be representative of emissions from single unique energy states in the QD.

By writing a simple simulation we can approximate what will happen when individual sharp peaks are spectrally resolved (or unresolved). The following sections will discuss the simulation, the physical parameters that were considered in the simulation, and the data gathered from several variations of the simulation. Results and the implications of the results will then be discussed.
4.2 Simulation parameters

A Mathematica program was written to predict the effects of spectrally resolved and unresolved (overlapped) sharp peaks. In this program (See Appendix A) energy values of 2.225 and 2.235 eV were chosen to match the peak of the experimentally determined broad feature. Around these mean values, a normal Gaussian distribution of values was generated with standard deviations of 0.015 and 0.023. The values for the standard deviation were chosen to be similar to the standard deviations used in the baseline fits for the PL spectra (refer to Section 3.3.1). The values in the normal distribution represent the energy distribution of the individual sharp peaks in the PL spectrum. In this way reductions in QD density corresponding to reductions in aperture areas can be simulated by reductions in the number of members in the normal distribution. A representation of such a distribution is provided in Figure 4.1. This

\[
\text{Gaussian} = \text{intensity} \times e^{-2.77259 \times (\text{center} + \text{energy})^2 / (\text{width}^2)} \quad (4.1)
\]
generates a distribution of energies that is most populated around the mean value. This is the type of distribution one would expect to be associated with PL from a distribution of individual quantum dots of similar size and composition (see section 3.3.3 and 3.4).

Individual sharp peaks are generated by an additional normal distribution of the form: which uses each value of the set of previously generated energies as a separate mean value. This provides for a sharp peak to be centered and expanded around each of the individual energy values. The (intensity) term controls the height while the

\[
\frac{-2.77259(\text{center} + \text{energy})^2}{(\text{width})^2}
\]

term controls the shape of the sharp peaks. For efficiency the program first separates the energy values into twelve overlapping bins. This is done by dividing the energy range established by the maximum and minimum energy values by twelve. This allows the intensity contribution from the overlap of each individual peak to be calculated in smaller groups. The intensity contribution is summed for each energy value from the minimum energy to the maximum energy in the bin by 0.0005 eV increments. In this way the superposition of overlapping peaks is accounted for in a time effective manner. A measured peak width of 250 µeV, obtained from the temperature dependence study (Chapter 2.2.2), and an arbitrary value of one for the individual peak intensity are the parameters used in the simplest form of the simulation. Different values for the intensity and the individual sharp peaks width will also be used to examine the effect that variations in the parameters have on the simulated spectra. This simulation models the effect that reducing the number of sharp peaks has on the spectral resolution (spectral sharp peak overlap) of the PL spectra.

### 4.3 Simple Simulation
Data from the simulation was used to demonstrate the effect of reducing the number of individual peaks of a PL spectrum. Starting from a large number of peaks guarantees overlap when the individual peaks are superimposed. Reducing the number of sharp peaks sampled simulates a reduction in aperture area. For this purpose the individual peak intensity (from equation 2.1) was set at unity and the peak shape was dictated by:

\[
\text{individual peak} = e^{-2.77259 \times (\text{center} + \text{energy})^2 / (\text{width})^2}
\]  

(4.2)

overlap when the individual peaks are superimposed. Reducing the number of sharp peaks sampled simulates a reduction in aperture area. For this purpose the individual peak intensity (from equation 2.1) was set at unity and the peak shape was dictated by: Where the width as measured from the experimental PL data is \(\sim 250 \mu\text{eV}\). This value was obtained from the 21.783 \(\mu\text{m}^2\) square aperture at 5 K. The term “center” refers to each of the random generated energies while the term “energy” refers to the value of the energy for which the contributions from all the overlapping peaks were summed. This simulation is carried out for different numbers of sharp peaks ranging from 50,000 to 200. The data from the simulation was then plotted using Origin and a smooth curve was fit to the baseline (see section 3.3.1 and appendix B for baseline fit details). The plots from this simulation are presented in Figures 4.2 through 4.6.
Figure 4.2: Simulated PL spectra composed of multiple individual peaks each with a FWHM= 250 µeV and an individual peak intensity of unity. (a) Simulation with 50,000 individual sharp peaks (b) simulation with 25,000 individual sharp peaks
Figure 4.3: Simulated PL spectra composed of multiple individual peaks each with a FWHM= 250 µeV and an individual peak intensity of unity (a) simulation with 12,500 individual sharp peaks (b) simulation with 6225 individual sharp peaks
Figure 4.4: Simulated PL spectra composed of multiple individual peaks each with a FWHM = 250 µeV and an individual peak intensity of unity (a) simulation with 3,112 individual sharp peaks (b) simulation with 1,556 individual sharp peaks
Figure 4.5: Simulated PL spectra composed of multiple individual peaks each with a FWHM= 250 µeV and an individual peak intensity of unity (a) simulation with 778 individual sharp peaks (b) simulation with 389 individual sharp peaks
These plots demonstrate that reducing the number of sharp peaks results in (1) a reduction in total spectral intensity, (2) a decrease in individual sharp peak overlap, and (3) a disappearance of the broad feature.

So that these results could be compared to the experimental PL results from Chapter 3, the integrated fractional intensity of the sharp and broad features were calculated using the same method used for the experimental PL data (see section 3.3.1). From this, we can examine how the sharp and broad features present in the simulated PL spectra (Figures 4.2 through 4.6) change in response to a reduction in the number of individual sharp peaks. These results (Figure 4.7), reveal that the broad feature completely disappears when the sharp peak density is reduced to approximately 200 sharp peaks. As we will see in Chapter 5, this is not consistent with the results obtained from a comparison of the

Figure 4.6: Simulated PL spectra composed of multiple individual peaks each with a FWHM= 250 µeV and an individual peak intensity of unity. The simulation contains 194 individual sharp peaks.
sharp/broad integrated fractional intensity from the CW PL experiment conducted through the apertures on the CdSe/ZnSe SAQD sample.

Figure 4.7: Results of the simple simulation of PL spectra composed of multiple individual peaks each with a FWHM= 250 µeV and an individual peak intensity of unity.

4.4 Simulation of increased peak width

Although the simple model presented in the previous section was successful in demonstrating the effect that reducing the number of sharp peaks has on the ratio of the
areas for the sharp and broad features, it also raises additional questions. Primarily, what if the disappearance of the broad feature was due to the choice for the initial value of the peak width? Experimentally, the peak width was found to be between 200 and 500 µeV in Chapter 3. To answer this question, peak widths of 100, 200, 300, 500, 1000, 2000, and 3000 µeV were sampled. The effect of increasing the term “width” for an individual peak is shown in Figure 4.8. Recall, the shape of the curve is regulated by the exponential term:

\[-2.77259(\text{center} + \text{energy})^2 / e^{(\text{width})^2}\]

**Figure 4.8:** The effect of increasing the value for the term “width” for an individual sharp peak. (a) the shape of individual peaks for different widths. (b) The increase in peak area with increased peak width

Increasing the value of this term increases the width of the curve with out affecting the intensity of the peak (Figure 4.8 a). Changing this value affects the area under each peak, which increases with an increase in width. The increase in individual peak area associated with increased peak width is presented in Figure 4.8 b.
To understand the effect that an increase in the spectral line width has on the superposition of the individual peaks, the simulation of the PL spectra were repeated multiple times accounting for different individual peak width energies. Peak width values of 100 $\mu$eV, 250 $\mu$eV, 500 $\mu$eV, 1000 $\mu$eV, and 3000 $\mu$eV represent the transition from a sharp narrow peak to a broad peak width each with an intensity of one. For each of these peak width values, 30000, 15000, 8000, 4000, 2000, 1000, 500, and 200 individual sharp peaks were sampled to represent the reduction in the number of sharp peaks. The results from this simulation are presented in Figures 4.9 through 4.12.
Figure 4.9: Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of unity (a) simulation with 30000 individual sharp peaks and FWHM= 100, 250, 500, 1000, and 3000 µeV (b) simulation with 30000 individual sharp peaks and FWHM= 100, 250, and 500 µeV
**Figure 4.10:** Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of unity (a) simulation with 8000 individual sharp peaks and FWHM= 100 and 250 μeV (b) simulation with 8000 individual sharp peaks and FWHM= 250, 500, and 1000 μeV
Figure 4.11: Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of unity (a) simulation with 2000 individual sharp peaks and FWHM= 100 and 250 μeV (b) simulation with 2000 individual sharp peaks and FWHM= 250, 500, and 1000 μeV
Figure 4.12: Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of unity (a) simulation with 200 individual sharp peaks and FWHM= 250, 500, and 1000 $\mu$eV (b) simulation with 200 individual sharp peaks and FWHM= 100, 250, 500, 1000, and 3000 $\mu$eV
The results from the simulated PL spectra (Figures 4.9 through 4.12) can also be presented in a qualitative manner. This will be done by examining the effect that changing the number of sharp peaks in the simulation has on both the intensity of the broad feature and the fractional integrated intensity. The results from these studies are presented in Figure 4.13.

The change in the fractional integrated area for the sharp and broad features of the simulated PL spectra were studied as a function of changing peak number for sharp peak widths of 100, 250, 500, 1000, and 3000 µeV. These results (Figure 4.13 b) show a similar behavior to the previous simulation for the 100 and 250 µeV peak widths but as the peak width is increased, the plots cease to diverge at ~ 1000 peaks as seen before (Figure 4.7). Further, the plot associated with the 3000 µeV peak widths is approximately horizontal and has a value slightly less than one. The differences between the 1000 and 3000 µeV peak width plots (Figures 4.9 through 4.12) and the experimental PL spectra (Figures 3.2 through 3.9) preclude this simulation from being adequate in describing the experimental PL spectra.

The intensity of the generated smooth baseline fit (see section 3.3.1) was also measured for each spectrum to determine the effect that changing the number of sharp peaks in the simulation has on the intensity of the broad feature. Plotting these results with respect to number of sharp peaks (Figure 4.13 a) shows that the plot for each of the peak widths is linear and has a positive slope. Interestingly, the increase in slope from a peak width of 100 to 3000 µeV (figure 4.13 a inlet) is also linear and has a steep slope. This steep slope can be attributed to an increase in area for the individual peaks widths (Figure 4.8) and is responsible for the broad feature not disappearing for peak widths of
Figure 4.13: results from simulated PL spectra (Figures 4.9 through 4.12) composed of multiple individual peaks with FWHM = 100, 250, 500, 1000, and 3000 µeV and an individual peak intensity of unity (a) plot of broad feature peak intensity with respect to the number individual sharp peaks (inlet) plot showing the steep slope of 500 A.U. intensity/1000 peaks (b) plot of the sharp/broad fractional integrated intensity as a function of the number of individual sharp peaks
500, 1000, and 3000 µeV in the simulated PL spectra (Figures 4.9 through 4.12). These results suggest that a term must be included in equation (2.2) that maintains a constant peak area for increased peak width.

4.5 Simulation of constant peak area and additional parameters

Up to this point the two simulations have been reasonably successful predicting trends in the experimental PL spectra for large individual peak densities while failing to be successful for small peak densities. The question that remains is: Is the prediction of the broad feature disappearance an artifact of the chosen parameters? To answer this question, additional physical parameters need to be included in the simulation. In the previous simulation the area of the individual peaks increased with an increase in linewidth. The increase in the peak area dominated the way the data responded to an increased peak width. To eliminate this effect, a scaling term was added to the intensity in the form (width/300 µeV). This term scales the peak intensity to maintain a constant area under each peak while increasing the linewidth. It also assumes that 300 µeV is the mean for the peak width (Figure 3.14 a). The effect of this is presented in Figure 4.14. The value of 1200 was also factored into the intensity to match the experimental value for the intensity of a single peak. This value was taken from the average intensity of peaks measured in the PL emissions from the CdSe/ZnSe SAQD with acquisition times of one second multiplied by 10 to match the 10 second acquisition times in Figures 3.2 through 3.9. Peak widths of 100, 300, 500, 1000, and 3000 µeV were then sampled to determine the effect of increased line width. The number of lines sampled for each width was
In the normal Gaussian distribution of the simulation a mean of 2.235 with a standard deviation of 0.027 replaced the old values of 2.225 with a standard deviation of 0.015. This centered the data closer to the true center value of the PL emissions. End points for the simulation data set were fixed at 2.163 eV and 2.3135 eV to simulate the range of values included in the PL spectra. The data was then generated by the Mathematica simulation and plotted using Origin (Figures 4.15 through 4.19).

Figure 4.14: The effect of the term width/300 µeV in the second simulation on (a) the shape and intensity of the individual peaks (b) the calculated area of the individual peaks.
Figure 4.15: Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of 1200*(width/300 \( \mu \text{eV} \)) (a) simulation with 12000 individual sharp peaks and FWHM= 100, 300, 500, 1000, and 3000 \( \mu \text{eV} \) (b) simulation with 12000 individual sharp peaks and FWHM= 300, 500, 1000 \( \mu \text{eV} \)
Figure 4.16: Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of 1200*(width/300 µeV) (a) simulation with 3000 individual sharp peaks and FWHM= 100, 300, 500, 1000, and 3000 µeV (b) simulation with 3000 individual sharp peaks and FWHM= 300, 500, 1000 µeV
Figure 4.17: Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of $1200 \times \frac{\text{width}}{300 \, \mu\text{eV}}$ (a) simulation with 800 individual sharp peaks and FWHM= 100, 300, 500, 1000, and 3000 $\mu\text{eV}$ (b) simulation with 800 individual sharp peaks and FWHM= 300, 500, 1000 $\mu\text{eV}$
Figure 4.18: Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of $1200 \times \text{width}/300 \, \mu\text{eV}$ (a) simulation with 200 individual sharp peaks and FWHM= 100, 300, 500, 1000, and 3000 $\mu\text{eV}$ (b) simulation with 200 individual sharp peaks and FWHM= 300, 500, 1000 $\mu\text{eV}$
Figure 4.19: Simulated PL spectra composed of multiple individual peaks each with an individual peak intensity of $1200 \times \text{width}/300 \, \mu \text{eV}$ (a) simulation with 50 individual sharp peaks and FWHM= 100, 300, 500, 1000, and 3000 \, \mu \text{eV} (b) simulation with 50 individual sharp peaks and FWHM= 300, 500, 1000 \, \mu \text{eV}
From Figure 4.15 through 4.19 several qualitative observations can be made. As in the first two simulations individual peak overlap and overall intensity decreases with a reduction in the number of sharp peaks. Also, plots from both the 100 and 3000 µeV widths do not match the experimental PL results (Figure 3.2 through 3.9). From a qualitative perspective, the 500 µeV peak width appears to be the only sampled peak width that supports a broad feature that does not disappear for low numbers of individual peaks and still maintains the appearance of the experimental PL (Figures 3.2 through 3.9). This possibility will be examined in Chapter 5 when these results are compared to the experimental results.

These observations can also be compared to quantitative results achieved by fitting a smooth curve to the base line and calculating the fractional integrated intensity for both the sharp and broad features. This analysis is consistent with all the previous analysis preformed on both the simulations and the experimental data (see Section 3.3.1). In addition to plotting the sharp divided by broad fractional integrated intensity, the trends
in the intensity of the fit smooth base line can also be plotted for each of the peak widths. The intensity analysis of the smooth base line fit (Figure 4.20), confirms that the strong dependence of the area of the individual peaks to the increase in peak width has been eliminated. All of the lines plotted for the intensity vs. number of peaks sampled have similar slopes. They also differ in intensity by a similar constant value, which is less than an order of magnitude between the 100 µeV and the 3000 µeV widths. From the result of the sharp vs. broad fractional integrated intensity (Figure 4.21), all of the peak widths except the 3000 µeV line increase by greater than two orders of magnitude. This is associated with a disappearance of the broad feature for small numbers of sampled peaks.

**Figure 4.20**: Relationship of the smooth baseline fit intensity to the increase in the number of sharp peaks.
Although the slope of the 3000 µeV line appears very horizontal, the shape of the plotted data eliminate considering it as a model for the experimental PL data.

Figure 4.21: Sharp/broad fractional integrated intensity from the simulation of the effect of increased individual peak width from 100 µeV to 3000 µeV.

The third simulation provides for three major additions not included in the first two simulations: (1) a constant area while increasing the width of each individual sharp peak. (2) a normal Gaussian distribution, modified to more accurately represent the value of the mean value from the PL emissions. (3) An intensity that is comparable to the experimental PL emissions from CdSe/ZnSe SAQD. These three additions provide useful information that will be compared with the experimental PL emissions from CdSe/ZnSe SAQD in Chapter 5.
Chapter 5
Comparison and discussion of experimental and simulated scaling properties

5.1 Objectives

In Chapters 3 and 4, a parallel has been established to study the scaling properties of the CdSe/ZnSe SAQD energy landscape as a function of varying aperture area. Chapter 3 discussed the effect of gathering PL through apertures of decreasing area. Chapter 4 simulated the effect of reducing the number of sharp peaks in a single discrete QD energy state model. This chapter will compare and discuss these results. A simulation that constructs a series of spectra composed of two distinct energy states will also be compared to the experimental PL results. A discussion will follow that focuses on the implications that arise when the sharp/broad fractional integrated intensity from the two energy state simulations are compared to the sharp/broad results from the experimental PL spectra.

5.2 Comparison of the sharp/broad areas

The simulations in Chapter 4 presented data based on the assumption that PL emissions from CdSe SAQD are composed of the spectral overlap of individual sharp peaks. If this were true the experimental spectra and the simulated spectra should be
identical. In Figure 5.1, the results from the simplest form of the simulation (Figure 4.7), are compared with the experimental PL results (Figure 3.12). This simulation is constructed from peaks with widths of 250 \( \mu \text{eV} \) and intensities of one. The important feature demonstrated by Figure 5.1 is the clear and abrupt change that takes place between the experimental PL and the simulation for aperture areas less than approximately \( 1 \mu \text{m}^2 \) (700 peaks). Comparing the data from the experiment to the simulation in this way shows that with approximately 500 individual sharp peaks the broad feature (assumed to be due to spectral overlap) in the simulation disappears. Note

![Figure 5.1](image-url): Comparison of the experimental PL data (Figure 3.12) and the results from the first simulation with a peak width of 250 \( \mu \text{eV} \) and an intensity of unity (Figure 4.7).
that the broad feature from the experimental data continue to be approximately equal to
the fractional area of the sharp peaks for apertures as small as $6 \times 10^{-3} \, \text{µm}^2$.

In the same way variations in peak width can be simulated and compared to
experimental results. The second simulation maintains an individual sharp peak intensity
of unity, increases individual sharp peak area with increased individual peak width, and
presents data for peak widths of 100, 250, 500, 1000, and 3000 µeV. The simulated
spectra (Figures 4.9 through 4.12) with peak widths of 1000 and 3000 µeV do not form
sharp peaks similar to the spectra obtained from the PL experiment (Figures 3.2 through
3.9) and need not be considered. Figure 5.2 presents a comparison of the sharp/broad
fractional area from the experimental PL spectra and the simulated spectra with
individual peak widths of 100, 250, and 500 µeV. In Figure 5.2, the simulated data
approximate the experimental results until reaching an aperture area of approximately
0.5µm² or a simulated peak density of 400 individual sharp peaks. Note that the 700
individual sharp peaks matches an aperture area $1 \mu m^2$ corresponding to a QD density of $\sim 700 \ \mu m^{-2}$ [7]. Each of the simulations demonstrate an abruptly deviation from the experimental data. This abrupt change can be attributed to the area contribution from the broad feature becoming much less than the contribution due to the sharp peaks.

In Chapter 5, a third simulation is constructed which takes into account more of the parameters of the experimental PL spectra (Figures 3.2 through 3.9). The third simulation (1) introduces an intensity of $\{1200 \times (\text{peak width}/300 \ \mu eV)\}$ to match intensities measured from the experimental data and maintain a constant area under the peaks and (2) presents data for peak widths of 100, 250, 500, 1000, and 3000 $\mu eV$ peak

**Figure 5.2:** Comparison of the experimental PL data from Figure 3.12 and results of the second simulation with a peak widths of 100, 250, and 500 $\mu eV$ and an intensity of unity in Figure 4.13.

In Chapter 5, a third simulation is constructed which takes into account more of the parameters of the experimental PL spectra (Figures 3.2 through 3.9). The third simulation (1) introduces an intensity of $\{1200 \times (\text{peak width}/300 \ \mu eV)\}$ to match intensities measured from the experimental data and maintain a constant area under the peaks and (2) presents data for peak widths of 100, 250, 500, 1000, and 3000 $\mu eV$ peak
widths. Comparing this third simulation to the experimental PL data confirms that the disappearance of the broad feature in the first two simulations is not due to factors such as poorly chosen intensities or peak areas. As in the first two simulations sharp peak features are not apparent in the simulated spectra for a peak width of 3000 µeV and will
not be considered further. Figure 5.3 displays the sharp/broad fractional area results from the experimental PL spectra and the simulation with individual peak widths of 100, 250, 500, and 1000 µeV.

**Figure 5.3:** Comparison of the experimental PL data from Figure 3.12 and results of the second simulation with a peak widths of 100, 250, and 500 µeV and an intensity of unity in Figure 4.13.

The plots (Figures 5.1, 5.2, and 5.3) comparing the sharp/broad fractional integrated intensity between the single energy state model and the experimental PL data demonstrate that all of the simulations fail to describe the experimental PL spectra for peak densities less than ~400 individual sharp peaks or aperture areas less than ~ 1 µm². This calls into question the validity of the single energy state model.
5.3 The multiple energy state model

An interesting result of the single energy state model simulation arises when two or more single data sets are combined to form a new spectrum. By adding the intensities at each point from two of these data sets, the effect of producing a spectrum due to multiple energy states can be achieved. In this way a simple version of the multiple energy state model can be examined.

To construct such multiple energy state spectra, data generated from individual peak widths of 300 and 3000 µeV from the third simulation (Section 4.5) are combined to produce a single set of spectra. This establishes a simple simulation of the PL emissions from two energy states, which can be compared to the experimental PL spectra. The advantage of using the simulation presented in Section 4.5 is that both changes in intensity and width for the individual peaks are included. The peak width of 300 µeV corresponds with the mean peak value (Figure 4.14 a) and the second peak width of 3000 µeV matches other experimental data (Section 1.4, [8]). The spectra are then analyzed using the following steps: (1) isolating the sharp peaks using a Mathematica program to fit a smooth baseline (Appendix B), (2) calculating the area under the sharp peaks, (3) subtracting this area from the total area to obtain the area due to the broad feature, and (4) calculate the area ratio of the sharp/broad spectra for the simulation. In this way, the results for the simulated PL spectra corresponding to the multiple energy state model can be compared to the experimental PL results.

Figures 5.4 through 5.8 present simulated spectra from the multiple energy state model, which can be compared to the experimental PL data (Figures 3.2 through 3.9).
In Figures 5.4 through 5.8, the blue baseline fit is calculated using the method described in Section 3.3.1. The simulation is the superposition of 300 µeV and 3000 µeV single peak emissions for 12000, 6000, 3000, 1500, 800, 400, 200, 100, and 50 individual peaks. The number of peaks in this multiple energy state simulation combines equal numbers of peaks from both single peak data sets. For example the multiple peak simulation for 12000 peaks refers to 12000 sharp peaks and 12000 broad peaks superimposed. This simple simulation assumes two unique peaks (one sharp, one broad) for each QD. As will be seen, there is a close similarity between the multiple energy state simulation and the experimental PL data.

![Figure 5.4: Multiple peak simulated CdSe/ZnSe PL spectra consisting of peak widths of 300 µeV and 3000 µeV and an intensity of 1200*(300/peak width). The last term regulates the intensity such that the peak area is constant for all choices of peak width. The number of individual sharp peaks is 12000.](image-url)
Figure 5.5: Multiple peak simulated CdSe/ZnSe PL spectra consisting of peak widths of 300 $\mu$eV and 3000 $\mu$eV and an intensity of $1200*(300/$peak width$)$. The last term regulates the intensity such that the peak area is constant for all choices of peak width. The number of individual sharp peaks are (a) 6000 multiple peaks and (b) 3000 multiple peaks.
Figure 5.6: Multiple peak simulated CdSe/ZnSe PL spectra consisting of peak widths of 300 µeV and 3000 µeV and an intensity of 1200*(300/peak width). The last term regulates the intensity such that the peak area is constant for all choices of peak width. The number of individual sharp peaks are (a) 1500 multiple peaks and (b) 800 multiple peaks.
Figure 5.7: Multiple peak simulated CdSe/ZnSe PL spectra consisting of peak widths of 300 µeV and 3000 µeV and an intensity of 1200*(300/peak width). The last term regulates the intensity such that the peak area is constant for all choices of peak width. The number of individual sharp peaks are (a) 400 multiple peaks and (b) 200 multiple peaks.
Figure 5.8: Multiple peak simulated CdSe/ZnSe PL spectra consisting of peak widths of 300 µeV and 3000 µeV and an intensity of 1200*(300/peak width). The last term regulates the intensity such that the peak area is constant for all choices of peak width. The number of individual sharp peaks are (a) 100 multiple peaks and (b) 50 multiple peaks.
Following the analysis done on all spectra (see Section 3.3.1) allows for the calculation of the ratio of the sharp/broad fractional area for each of the 300 µeV + 3000 µeV simulated spectra. When the sharp/broad fractional area for the simulation is plotted and compared to the experimental PL data (Figure 3.12) both have very similar slopes and vary only slightly in magnitude. This demonstrates that the multiple energy state simulation and the experimental PL data are comparable in the way that the area of the broad feature scales to the area of the sharp peaks. In addition, while the Mathematica simulation fails to describe the experimental PL data for the single energy state model, it describes the experimental PL data very well with a multiple energy state model. This,

![Figure 5.9: Comparison of the sharp/broad fractional area between the experimental PL data and the 300 µm + 3000 µm individual peak width simulation of the multiple energy states.](image-url)
combined with the data presented in Section 1.4 strongly suggests that the CdSe/ZnSe energy landscape is composed of multiple energy states rather than the superposition of a large number of single energy states.
Chapter 6
Summary

Photoluminescence from a CdSe/ZnSe SAQD sample was studied through a variety of apertures to determine the effect of a reduction in aperture area (Number of QD sampled). The apertures ranged from ~ 21 – 0.006 µm². The results of this experiment indicate that reductions in aperture area were accompanied by a reduction in PL emission intensity and a decrease in spectral overlap of the individual sharp peaks. These effects can be attributed to a reduction in the number of quantum dots sampled. Importantly, the PL emission spectra suggest that both the sharp peak features and the broad features persist at approximately equal integrated areas for all the aperture sizes sampled (Figure 3.12). This is inconsistent with a single energy state model were the PL emission spectra are the result of the spectral overlap of a great many individual sharp peaks.

Several simulations were constructed using Mathematica that model a single energy state explanation for the experimental PL spectra. These simulations were constructed and compared to the experimental PL results by comparing the ratio of the sharp/broad fractional integrated intensity (Figures 5.1, 5.2, and 5.3). These simulations increased in complexity with the first using an individual peak intensity equal to 1 and an individual peak width equal to 250 µeV. The width was chosen to correspond with previous data [8] and the intensity was chosen arbitrarily. The second simulation considers variation that arises from increasing the sharp peak width. Thus, individual peak widths were studied ranging from 100 – 3000 µeV all with intensity equal to 1. As a result of
increased peak width, the individual peak area also increased. The third simulation generated data corresponding to individual peak widths ranging from 100 – 3000 µeV but maintained a constant peak area for the entire range of widths. To lend reliable parameters to the third simulation, values for the intensity were determined experimentally. The individual peak intensity was determined to be ~ 1200 (A.U.) from the mean value shown in the plot of the individual sharp peak density with respect to aperture area (Figure 3.14 b). The 1 second PL accumulation time, in Figure 3.14, is accounted for by multiplying the results by ten. In all three simulations the generated spectra diverged from the experimental results for peak densities greater than ~ 1000 or aperture areas greater than ~ 1 µm² (Figures 5.1, 5.2, and 5.3). This result is inconsistent with the single energy state model.

Finally, the set of simulated spectra generated for the 300 µeV and 3000 µeV individual peak widths from the third simulation were combined in a simple additive manner. The resulting simulation is the superposition of the two simulated spectra and represents a simple version of a multiple energy state model were each quantum dot would emit from two distinct energy states. By the same method previously employed (Section 3.3.1), these new 300 µeV + 3000 µeV combined spectra were analyzed to determine the area associated with the sharp and broad features. When the ratio of the sharp/broad fractional integrated intensity was compared with the results from the experimental PL spectra (Figure 3.12) they were found to be approximately equal in value and slope. The results from this simulation (Figure 5.9) suggest that a multiple energy state model does describe the experimental CdSe/ZnSe SAQD PL spectra.
References

Appendix A

Calculation of sphere density

Calculation of the number of spheres/volume for all five sphere sizes.

\[
\text{olddensity}_1 = \frac{(1.58553 \times 10^6) \times \text{(spheres)}}{\text{drop}} \times \frac{(171 \times \text{drop})}{5 \times \text{ml}}
\]
\[5.42251 \times 10^7 \text{ spheres/ml}\]

\[
\text{olddensity}_2 = \frac{(3.32449 \times 10^6) \times \text{(spheres)}}{\text{drop}} \times \frac{(171 \times \text{drop})}{5 \times \text{ml}}
\]
\[1.13698 \times 10^8 \text{ spheres/ml}\]

\[
\text{olddensity}_3 = \frac{(9.4455 \times 10^6) \times \text{(spheres)}}{\text{drop}} \times \frac{(171 \times \text{drop})}{5 \times \text{ml}}
\]
\[3.23036 \times 10^8 \text{ spheres/ml}\]

\[
\text{olddensity}_4 = \frac{(3.16964 \times 10^7) \times \text{(spheres)}}{\text{drop}} \times \frac{(171 \times \text{drop})}{5 \times \text{ml}}
\]
\[1.08402 \times 10^9 \text{ spheres/ml}\]

\[
\text{olddensity}_5 = \frac{(2.76693 \times 10^8) \times \text{(spheres)}}{\text{drop}} \times \frac{(171 \times \text{drop})}{5 \times \text{ml}}
\]
\[9.4629 \times 10^9 \text{ spheres/ml}\]

Calculation of the number of spheres/drop of liquid for five different sphere sizes.

\[
\text{mixture}_1 = \frac{\text{olddensity}_1}{10} \times \frac{5 \times \text{ml}}{158553. \text{ spheres/drop}}
\]

\[
\text{mixture}_2 = \frac{\text{olddensity}_2}{10} \times \frac{5 \times \text{ml}}{332449. \text{ spheres/drop}}
\]

\[
\text{mixture}_3 = \frac{\text{olddensity}_3}{10} \times \frac{5 \times \text{ml}}{108402 \times \text{ spheres/drop}}
\]


\[
\text{spheres} = \frac{\text{mixture}_4 \text{ old density}_4 \times 5 \times \text{ml}}{10 \times (171 \times \text{drop})}
\]
\[
3.16964 \times 10^6 \text{ spheres}
\]

\[
\text{spheres} = \frac{\text{mixture}_5 \text{ old density}_5 \times 5 \times \text{ml}}{10 \times (171 \times \text{drop})}
\]
\[
2.76693 \times 10^7 \text{ spheres}
\]

Calculation of the number of spheres/50 area (assumes dried drop diameter)

\[\text{area} = \pi \times \left( \frac{0.75 \times 10^{-2} \times \text{m}}{2} \right)^2\]

\[
0.0000441786 \text{ m}^2
\]

\[
\text{spheres} = \frac{\text{mixture}_1 \text{ drop} \times \text{m}^2 \times (50 \times \mu \text{m})^2}{\text{area} \times (10^6 \times \mu \text{m})^2}
\]

\[
8.97226 \text{ spheres}
\]

\[
\text{spheres} = \frac{\text{mixture}_2 \text{ drop} \times \text{m}^2 \times (50 \times \mu \text{m})^2}{\text{area} \times (10^6 \times \mu \text{m})^2}
\]

\[
18.8128 \text{ spheres}
\]

\[
\text{spheres} = \frac{\text{mixture}_3 \text{ drop} \times \text{m}^2 \times (50 \times \mu \text{m})^2}{\text{area} \times (10^6 \times \mu \text{m})^2}
\]

\[
53.4506 \text{ spheres}
\]

\[
\text{spheres} = \frac{\text{mixture}_4 \text{ drop} \times \text{m}^2 \times (50 \times \mu \text{m})^2}{\text{area} \times (10^6 \times \mu \text{m})^2}
\]

\[
179.365 \text{ spheres}
\]

\[
\text{spheres} = \frac{\text{mixture}_5 \text{ drop} \times \text{m}^2 \times (50 \times \mu \text{m})^2}{\text{area} \times (10^6 \times \mu \text{m})^2}
\]

\[
1565.76 \text{ spheres}
\]
Appendix B

Monte Carlo simulation of PL spectrum

```mathematica
Exit[] << Statistics`NormalDistribution`
ndist = NormalDistribution[2.235, 0.023]

Elist = Table[Random[ndist], {i, 1, 12000}];

Max[Elist]
2.31598

Min[Elist]
2.13296

EBreak = Table[Min[Elist] + i*(Max[Elist] - Min[Elist])/12, {i, 0, 12}]
{2.13296, 2.14821, 2.16346, 2.17871, 2.19397, 2.20922, 2.22447, 2.23972, 2.25497, 2.27022, 2.28548, 2.30073, 2.31598}

ListPlot[Elist];

Clear[gaussline, intensity, center, width]

gaussline[intensity_, energy_, center_, width_] = intensity*Exp[-(energy - center)^2/(0.5*width/0.832555)^2]

fwhm = 0.003
0.003
```
P1Elist = Select[Elist, EBreak[[1]] - (fwhm * 2) < #1 < EBreak[[2]] + (fwhm * 2) &];
P2Elist = Select[Elist, EBreak[[2]] - (fwhm * 2) < #1 < EBreak[[3]] + (fwhm * 2) &];
P3Elist = Select[Elist, EBreak[[3]] - (fwhm * 2) < #1 < EBreak[[4]] + (fwhm * 2) &];
P4Elist = Select[Elist, EBreak[[4]] - (fwhm * 2) < #1 < EBreak[[5]] + (fwhm * 2) &];
P5Elist = Select[Elist, EBreak[[5]] - (fwhm * 2) < #1 < EBreak[[6]] + (fwhm * 2) &];
P6Elist = Select[Elist, EBreak[[6]] - (fwhm * 2) < #1 < EBreak[[7]] + (fwhm * 2) &];
P7Elist = Select[Elist, EBreak[[7]] - (fwhm * 2) < #1 < EBreak[[8]] + (fwhm * 2) &];
P8Elist = Select[Elist, EBreak[[8]] - (fwhm * 2) < #1 < EBreak[[9]] + (fwhm * 2) &];
P9Elist = Select[Elist, EBreak[[9]] - (fwhm * 2) < #1 < EBreak[[10]] + (fwhm * 2) &];
P10Elist = Select[Elist, EBreak[[10]] - (fwhm * 2) < #1 < EBreak[[11]] + (fwhm * 2) &];
P11Elist = Select[Elist, EBreak[[11]] - (fwhm * 2) < #1 < EBreak[[12]] + (fwhm * 2) &];

intensity = 1200 * \frac{0.0003}{\text{fwhm}}

120.
Clear[SimLine]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P1Elist[[i]], fwhm], {i, 1, Length[P1Elist]}] /;
    EBreak[[1]] ≤ energy < EBreak[[2]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P2Elist[[i]], fwhm], {i, 1, Length[P2Elist]}] /;
    EBreak[[2]] ≤ energy < EBreak[[3]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P3Elist[[i]], fwhm], {i, 1, Length[P3Elist]}] /;
    EBreak[[3]] ≤ energy < EBreak[[4]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P4Elist[[i]], fwhm], {i, 1, Length[P4Elist]}] /;
    EBreak[[4]] ≤ energy < EBreak[[5]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P5Elist[[i]], fwhm], {i, 1, Length[P5Elist]}] /;
    EBreak[[5]] ≤ energy < EBreak[[6]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P6Elist[[i]], fwhm], {i, 1, Length[P6Elist]}] /;
    EBreak[[6]] ≤ energy < EBreak[[7]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P7Elist[[i]], fwhm], {i, 1, Length[P7Elist]}] /;
    EBreak[[7]] ≤ energy < EBreak[[8]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P8Elist[[i]], fwhm], {i, 1, Length[P8Elist]}] /;
    EBreak[[8]] ≤ energy < EBreak[[9]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P9Elist[[i]], fwhm], {i, 1, Length[P9Elist]}] /;
    EBreak[[9]] ≤ energy < EBreak[[10]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P10Elist[[i]], fwhm], {i, 1, Length[P10Elist]}] /;
    EBreak[[10]] ≤ energy < EBreak[[11]]
SimLine[energy_] :=
    Sum[gaussline[intensity, energy, P11Elist[[i]], fwhm], {i, 1, Length[P11Elist]}] /;
    EBreak[[11]] ≤ energy < EBreak[[12]]
SimLine[energy_] := 0
Export["Sime12000.txt", Table[{energy, SimLine[energy]}, {energy, 2.14, 2.33, 0.00005}], "Table"]
Sime12000.txt
Mathematica spectral baseline fit program

Initialization Stuff

<< Statistics`NonlinearFit`
ReadData::usage = "ReadData[n, filename, options]
reads data from from the file filename.
The first n words in the file are dropped.
ReadData takes the same options as ReadList"
ReadData[dropwords_Integer, filename_String, opts__] :=
Module[{inline, result}, inline = OpenRead[filename];
  Read[inline, Table[String, {dropwords}]];
  result = ReadList[inline, opts];
  Close[inline];
  result]
ReadData[n, filename, options] reads data from from the
file filename. The first n words in the file are
dropped. ReadData takes the same options as ReadList

? ToFileName
ToFileName["directory", "name"] assembles a full file name
from a directory name and a file name. ToFileName[
 {dir1, dir2, ... }, name] assembles a full file name
from a hierarchy of directory names. ToFileName[
 {dir1, dir2, ... }] assembles a single directory
name from a hierarchy of directory names. *More...

$TopDirectory
Applications: Mathematica 4.1 Files
SetDirectory["ZIP-100:Simulation 6-20-01:250ueV:"
ZIP-100:Simulation 6-20-01:250ueV

names = FileNames["*.txt"]
{simb1000.txt, simb15000.txt, simb2000.txt, simb200.txt,
simb30000.txt, simb4000.txt, simb500.txt, simb8000.txt}
names
{simb1000.txt, simb15000.txt, simb2000.txt, simb200.txt,
simb30000.txt, simb4000.txt, simb500.txt, simb8000.txt}

Test Case

Clear[data]
Table[data[i] = Partition[ReadData[0, names[[i]], Number],
  2], {i, 1, Length[names]}];
Take[data[1], {1, 10}]
{(2.17005, 0), {2.1701, 0}, {2.17015, 0}, 
{2.1702, 0}, {2.17025, 0}, {2.1703, 0},
{2.17035, 0}, {2.1704, 0}, {2.17045, 0}, {2.1705, 0}}
plot0 = ListPlot[data[1], PlotJoined -> True]

- Graphics -

test = Table[(Random[], Random[]), {i, 1, 101}];
Floor[Length[data[1]]]
2199
Ceiling[Length[data[1]] / 100]
22
testdata = Partition[data[1], Floor[Length[data[1]] / 100]]; 
Dimensions[testdata]
{104, 21, 2}
sortedData = Map[Take[#, Ceiling[Floor[Length[data[1]]] / 100] / 5] &, 
Map[Sort, testdata /. (x_, y_) -> (y, x)] /. (x_, y_) -> (y, x)]; 
CalculatedData = Map[Apply[Plus, #] &, sortedData] / 
Length[sortedData[[2]]];
plot1 = ListPlot[CalculatedData]

- Graphics -

Clear[A, x, σ];
curve = NonlinearFit[CalculatedData, A Exp[-σ (x - x0)^2], 
  x, {(A, Max[CalculatedData], 0, 10), (x0, 2.23, 2, 3), 
  (σ, 1000, 250, 5000)}, ShowProgress -> True]
Iteration: 1 ChiSquared: 394.02239767188144
   Parameters: {6.02549, 2.23, 1000.}
Iteration: 2 ChiSquared: 62.13179675898636
   Parameters: {4.01421, 2.22606, 1496.47}
Iteration: 3 ChiSquared: 42.769999800751556
   Parameters: {4.38507, 2.22522, 2330.21}
Iteration: 4 ChiSquared: 41.7818284637985
   Parameters: {4.4815, 2.22567, 2588.81}
Iteration: 5 ChiSquared: 41.77576174777076
   Parameters: {4.48487, 2.22573, 2598.47}
Iteration: 6 ChiSquared: 41.77571448888274
   Parameters: {4.48575, 2.22573, 2600.45}

\[4.48573 e^{-2600.4 (-2.22573 x)^2}\]

First[CalculatedData][[1]]
2.17015

Last[CalculatedData][[1]]
2.2783

plot2 =
   Plot[curve, \{x, First[CalculatedData][[1]],
   \[Last[CalculatedData][[1]]\}], PlotStyle \rightarrow \text{RGBColor[1, 0, 0]},
   \text{PlotRange} \rightarrow \text{All}]

- Graphics -
   Show[plot1, plot2]

Exportdata = plot2[[1, 2, 1]];  
ListPlot[Exportdata]

113
As a loop

SetDirectory["ZIP-100:Simulation 6-20-01:500ueV:"

names = FileNames["*.txt"]

ZIP-100:Simulation 6-20-01:500ueV
{ :simc1000.txt, :simc15000.txt, :simc2000.txt, :simc200.txt, 
: simc30000.txt, :simc4000.txt, :simc500.txt, :simc8000.txt}
Clear[data, A, \(\sigma\), x0, testdata, sortedData, CalculatedData, curve]

Table[data[i] = Partition[ReadData[0, names[[i]], Number], 2], {i, 1, Length[names]}];

Do[
    plot0 = ListPlot[data[i], PlotJoined -> True,
        DisplayFunction -> Identity];
    testdata[i] = Partition[data[i], Floor[Length[data[i]] / 100]];
    sortedData[i] = Map[Take[#, Ceiling[Floor[Length[data[i]] / 100] / 5]] &,
        Map[Sort, testdata[i] / {x_, y_} \[Rule] (y, x)] /.
        {x_, y_} \[Rule] {y, x}];
    CalculatedData[i] = Map[Apply[Plus, #] &, sortedData[i] / Length];
    curve = NonlinearFit[CalculatedData[i], A Exp[-\(\sigma\) (x - x0)\(^2\)],
        x, {{A, Max[CalculatedData[i]] + 2}, {x0, 2.23, 1.4, 3.5},
        \{\sigma, 1000, 250, 5000\}}];
    plot2 = Plot[curve, {x, First[CalculatedData[i]][[1]],
        Last[CalculatedData[i]][[1]]},
        PlotStyle -> RGBColor[1, 0, 0], PlotRange -> All,
        DisplayFunction -> Identity];
    Show[plot0, plot2, DisplayFunction -> $DisplayFunction];
    Exportdata = plot2[[1, 2, 1, 1]]; Export[SymbolReplace[names[[i]], "txt" -> "dat"], Exportdata, "Table"], 
    {i, 1, Length[names]}]