CONDUCTING NANOCRYSTAL SOLIDS
FOR
OPTOELECTRONIC DEVICES

by

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Graduate Department of The Edward S. Rogers Sr. Department of
Electrical and Computer Engineering
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Abstract

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Nanocrystal solids represent an exciting new class of materials. These are often referred to as “artificial solids”, in which the nanocrystals take the place of atoms in traditional solids.

This thesis reports the utility of field-effect transistor measurements to elucidate charge transport parameters, such as charge carrier density and charge carrier mobility in a nanocrystal solid. The evolution of these parameters with chemical treatments is followed and correlated to improved performance in photovoltaic devices. Chemical treatments are demonstrated to simultaneously engineer interparticle spacing, doping and electronic coupling in nanocrystal solids. The nanocrystal solids are then utilized as building blocks for fabricating all nanocrystal heterostructure. A type-I nanocrystal heterostructure is fabricated to demonstrate efficient electroluminescent device in the infrared communications wavelength. The device emits at peak wavelength of 1.58 \( \mu \text{m} \) with an efficiency of 0.5%.
This thesis represents the culmination of sixteen months of research. There is no doubt that I would simply have not made it to this stage without the guidance and support of exceptional people.

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Chapter 1

Introduction

1.1 Context

Solution-processed colloidal nanocrystals offer promising performance in applications as diverse as optical detection [9], solar power conversion [10], and light emission [11]. The motivation behind solution-processed devices is their low cost, large device area, physical flexibility and convenient materials integration compared to the conventional epitaxially grown, lattice-matched, crystalline semiconductor devices [12].

A key problem in computing today is the lack of an optical source that can be conveniently integrated with silicon electronics. Such a source is necessary to realize optical interconnects to link together increasingly high-speed electronic transistors. The materials from which electrically-injected lasers are traditionally made - compound semiconductors - are incompatible with growth on silicon. The possibility of a silicon nanocrystal laser [13] has generated huge excitement, but has led to optical gain alone, and never yet to lasing. Silicon lasers based on Raman gain [14] have recently generated excitement as well; yet these nonlinear optical devices provide no route to electrically-injected lasing.

Colloidal semiconductor nanocrystals offer the potential of tunable emissive properties and solution processability. These properties have been exploited to generate the first
observation of optically pumped lasing in a solution-processed infrared device [15]. However, the impact of these devices will be not realized unless gain is demonstrated through electrical injection. To date, the most efficient nanocrystal based electroluminescent [EL] device demonstrated has an efficiency of ~2% in the visible spectrum [16], while the reported near-infrared (1-1.3 \( \mu \text{m} \)) devices have efficiencies of less than 0.5% [17–19]. To date, there have been no demonstrations of efficient infrared emitting device at the telecommunication wavelength of 1.55 \( \mu \text{m} \). Furthermore, the aforementioned devices utilize organic semiconductors, which degrade under moisture and oxygen and therefore have limited operating lifetimes.

PbS nanocrystals are an ideal choice as an active material for the infrared wavelengths, since the bulk bandgap falls at 3 \( \mu \text{m} \), and through crystal size variation (quantum confinement), the absorption edge can be tuned from anywhere between 1700 to 950 nm [20]. This coupled with recent improvements in the electronic transport properties of colloidal nanocrystal films [12], motivates research for the development of optoelectronic devices from this material system.

### 1.2 Introducing Nanocrystal Solids

If a nanocrystal quantum dot is viewed as an “artificial atom”, then a superlattice of nanocrystals, by analogy, can be refereed to as “artificial solid”. In literature, this artificial solid has been reported under different terminologies, such as nanocrystal arrays, nanocrystal superlattice, nanocrystal solid, or nanocrystal thin films. In this report, the system will be referred to as nanocrystal solids. Some of the different means for preparing nanocrystal solids from solution processable colloidal nanocrystals are schematically illustrated in Figure 1.1. The question of interest here is what kind of collective properties arise when semiconductor nanocrystals are assembled into close-packed three dimensional solids. Essentially these material systems provide a dream test bed for condensed matter
Figure 1.1: Different means for preparing nanocrystal solids. [1]
physicists. Typical solids are classified into metals, insulators and semiconductors according to their electronic properties. There is essentially a very limited degree of control as the fundamental unit of these solids, namely atoms, cannot be modified. However, in the case of nanocrystal solids, the fundamental unit is a nanocrystal quantum dot, which has been shown to be tuned in limitless configurations because of the associated degrees of freedoms. One such “artificial tuning”-related aspect of these nanocrystal solids is that the bandgap may be controlled in at least two different ways. The first is through the dependence of energy levels in a nanocrystal on its dimensions. The second way is to reduce the distance between nanocrystals in the solid to increase quantum mechanical overlap [21]. In addition to the bandgap, the relative position of the fermi energy level in a semiconductor is also a very important parameter. The fermi energy level corresponds to the doping level of the semiconductor and thus there is significant motivation in engineering the doping level of nanocrystals.

1.3 Doping Semiconductor Nanocrystal Solids

Doping, defined as the intentional introduction of impurities into a material, is fundamental to controlling the properties of bulk semiconductors. Furthermore, it is also a crucial determinant of device properties ranging from transistor gain and photodetector sensitivity to the built-in voltage in junction devices. This has stimulated similar efforts to dope semiconductor nanocrystals. Most of the current efforts in doping nanocrystals follow the typical conventional route of incorporating dopants into the bulk of the nanoparticles either during nanoparticle synthesis or through post-processing of films. CdSe nanocrystal solids were modified from intrinsic to n-type through evaporation of potassium in high vacuum [22]. However, an inherent limitation of this method is that diffusion of the dopant in the film can only be applied to very thin films of approximately six monolayers. The incorporation of dopants during the synthesis process has
also encountered significant setbacks and has led to the hypothesis that nanoparticles self-purify during growth [23]. While electrochemistry and charge transfer doping in CdSe [22] and Au nanocrystals [24] respectively have shown strong net doping changes over multiple orders of magnitude, the materials presented limited stability. Recently, a hybrid organic-inorganic route to doping nanocrystal solids was demonstrated through the use of hydrazine [12]. PbSe nanocrystal solids were tuned between n-type, intrinsic and p-type doping. Although the materials were still not stable as hydrazine was reported to desorb over course of few hours, the process itself has great potential. The electron mobility for these hydrazine treated PbSe nanocrystal solids was reported to be $\sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is significantly better than most organic polymers and approaches the mobilities in amorphous hydrogenated silicon. In this work, several routes to doping PbS and PbSe nanocrystal solids will be described.

1.4 Field Effect Transistors

The invention of the first field effect device was conceived by Lilienfeld in his 1934 patent and later studied by Shockley and Pearson in 1948. It took thirty years before the concept was turned into a device, namely the metal-oxide-semiconductor field-effect transistor (MOSFET) by P.K. Wiemer at the RCA laboratories in 1964. Since then, MOSFETs have been omnipresent in the electronics industry from computer processors to other microelectronic devices. The advent of thin film transistors emerged from applications in the display technology and in the past 15 years have become ubiquitous in the electronic flat panel industry. Amorphous silicon has been the material of choice for thin film transistors, which is more a matter of economics than physics. [25]

However, there have recently been significant efforts in developing thin film field-effect transistors from novel materials such as organic polymers [25], inorganic nanowires and nanocrystals [26] and carbon nanotubes [27]. While the performance of devices made
from these novel materials is not up to par with the inorganic crystalline semiconduc-
tors, the motivation in pursuing these devices stems from cheaper fabrication costs and
improved processibility. These reasons can lead to a new niche of applications such as
electronic bar codes and identification tags. It is evident that field-effect transistors
fabricated from novel materials serve significant technological interest. However, a very
important application of these devices is often missed, as they can also be utilized to
extract charge transport parameters of materials. Therefore, in this study, the evolution
of charge transport parameters, particularly the doping level in nanocrystal solids will
be characterized through field-effect measurements.

1.5 Semiconductor Heterostructures

Semiconductor heterojunctions were first envisioned by Gubanov, Schokley and Herbert
Kroemer more than fifty years before back in 1950’s. However, the practical implementa-
tion of heterojunction devices was not reported until the development of new deposition
techniques, first liquid phase epitaxy and then followed with molecular beam epitaxy
(MBE) and metal-oxide chemical vapor deposition (MOCVD). The development of the
physics and technology of semiconductor heterostructures has revolutionized modern day
optoelectronics. Some of the devices that have resulted from semiconductor heterostruc-
tures include lasers, light emitting diodes, solar cells and photodetectors. [28]

The advent of heterostructure based devices has almost always resulted from a novel
processing idea as described earlier. The conventional heterostructure processing of in-
organic crystalline semiconductors requires a stringent condition of lattice matching at
the interface. Thus only a selected range of semiconducting material can be utilized.
Solution processed heterostructures fabricated from materials such as organic polymers
or colloidal nanocrystals require no lattice matching conditions. There have been several
successful developments of optoelectronic devices from solution processed heterostruc-
Ch 1. Introduction

features. A nanocrystal-organic polymer heterostructure has been previously utilized to fabricate light-emitting diodes [11] and photovoltaic devices [29]. In this study, a novel fabrication route to building all-nanocrystal heterostructures will be described. The heterostructure will be used to develop infrared light emitting diodes.

1.6 Thesis Goals

The scope of this thesis is to study and engineer key charge transport parameters of nanocrystal solids.

In addition, a general approach to building nanocrystal heterostructures from nanocrystal solid is presented. This work aims to gain insight on the physics behind the chemical treatments performed on nanocrystal solids. The resulting knowledge will be advantageous in answering fundamental questions for existing devices, but more importantly, it will also provide a pathway to novel and efficient device architectures.

1.6.1 Thesis Questions

The scope of the thesis statement could take several volumes to cover completely. Therefore, in order to present the thesis objectives into a more manageable task, the following fundamental questions are presented:

1. How does an electron move in a nanocrystal solid?

2. What are the key charge transport parameters for a nanocrystal solid?

3. How can these charge transport parameters be reliably characterized?

4. How to engineer the charge transport parameters of PbS and PbSe nanocrystal solids?

5. What are some of the other applications of nanocrystal solids?
6. How to build an electroluminescent device from nanocrystal heterostructures?

The first two questions will be addressed through a theoretical analysis of the literature, while the remaining questions will be explored through experimental analysis. The thesis is organized such that each chapter is devoted to answering one or multiple of these questions.

1.7 Thesis Organization

In chapter 2, the relevant charge transport models for nanocrystal solids are presented. An analytical description for the size tunable properties of a nanocrystal is provided, followed by the discussion on different transport regimes in nanocrystal solids. The operating principles and fabrication process for a thin film field-effect transistor are described in chapter 3. The field effect transistor measurements are utilized to characterize charge carrier mobility and charge carrier density in nanocrystal solids. The engineering and characterization of these two parameters are presented in chapter 4. These nanocrystal solids are then utilized as building blocks for an all nanocrystal heterostructure. The fabrication procedures for building a generic nanocrystal heterostructure is presented in chapter 5. This also includes fabrication of an efficient infrared light emitter for a variety of applications. Finally, chapter 6 provides a summary of the work. The contributions to the field are noted and future research directions are speculated. For the supplementary material, Appendix A provides the ligand exchange procedure employed for PbS nanocrystal solids. Appendix B describes the photolithography procedure utilized in patterning field-effect transistor devices.
Chapter 2

Nanocrystal Solids: Review and Theory

2.1 Introduction

A unifying theme in nanoscience is that size and shape are important. It is often challenging to understand the implications of size-tunable properties when working with the intermediate length scale characteristics of many nanomaterials, such as nanocrystals [3]. The number of electrons present even in a single nanocrystal makes it almost impossible to perform molecular-type electronic calculations. Therefore, instead of presenting a computationally intensive approach, it would be helpful if the bulk theory could be modified and extended in order to describe nanostructures and provide analytical results. In this chapter, the powerful concepts developed in condensed matter physics will be applied to explain the electronic characteristics of nanocrystals and nanocrystal solids.

2.2 Nanocrystal Quantum Dot

A nanocrystal is either a metal or semiconductor shrunk down in dimensions to the nanoscale regime. The nanoscale regime for a semiconductor is defined analogously to an
electron in a potential well. The electron in a potential well is defined to be quantum confined when the width of the well approaches the length scale of an electron, which could be either its DeBroigle wavelength or mean free path. Similarly for the semiconductor, quantum confinement occurs when the excitonic Bohr radius, which is the length scale of an exciton, is of the order of the semiconductor dimensions. An exciton is a quasi-particle that forms where Coulomb-interacting electrons and holes in semiconductors are bound into pair states. In this section, a modified version of the conventional effective mass approach is utilized to elucidate quantum size effects in semiconducting nanocrystals.

2.2.1 Particle-in-a-Sphere

Consider an arbitrary particle of mass $m_0$ inside a spherical potential well of radius $a$, where:

$$V(r) = \begin{cases} 0, & r < a \\ \infty, & r > a \end{cases}$$

(2.1)

The symmetry of this problem yields eigenfunctions to the Schrodinger equation, which are similar to the atomic-like orbitals. These eigenfunctions are labeled by the quantum numbers $n(1, 2...), l(s, p, d,)$ and $m$. The energies are identical to the kinetic energy of the free particle, except that the wave vector, $k_{nl}$, is quantized by the spherical boundary conditions. Following are the solutions to this boundary value problem. [2]

$$\text{Eigenfunctions} : \Phi_{n,l,m}(r, \theta, \phi) = C \frac{j_l(k_{nl}, r)}{r} Y^m_l(\theta, \phi)$$

(2.2)

where $C$ is a normalization constant, $j_l$ is the $l$th-order spherical Bessel function, and $Y^m_l$ is a spherical harmonic.

$$\text{Discrete Wavevector} : k_{nl} = \frac{\alpha_{n,l}}{a}$$

(2.3)
Energy Eigenvalues: \[ E_{n,l} = \frac{\hbar^2 k_{n,l}^2}{2m_0} = \frac{\hbar^2 \alpha_{n,l}^2}{2m_0 a^2} \] (2.4)

### 2.2.2 Effective Mass Approach

At a first glance, the model developed in the previous section may not seem useful for the nanocrystal problem, because the sphere is not empty, but filled with semiconducting atoms. Just as in bulk semiconductor solids, the atoms in the crystal will be accounted for by introducing Bloch wavefunctions:

\[ \Psi(\vec{r}) = \sum_k C_{n,k} u_{n,k}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \] (2.5)

where the free electron wave is modulated by \( C_{n,k} \), the expansion coefficients, which ensure that the sum satisfies the spherical boundary conditions; and \( u_{n,k} \), the periodic potential accounting for atoms. If it assumed that the \( u_{n,k} \) has a weak dependence on \( k \), then Equation 2.5 can be rewritten as:

\[ \Psi(\vec{r}) = u_{n,0}(\vec{r}) \sum_k C_{n,k} e^{i\vec{k} \cdot \vec{r}} = u_{n,0}(\vec{r}) f(\vec{r}) \] (2.6)

where \( f(\vec{r}) \) is the atomic wavefunction, which was obtained from the particle in the sphere; and \( u_n \) is the envelope wavefunction, which is derived from the periodic lattice potential (either using the free-electron or tight binding models). The energy of these levels is the same as that from the particle in a sphere model, with the free particle mass \( m_0 \) replaced by the effective mass, \( m^* \) in Equation 2.4. The details of this discussion are illustrated in Figure 2.1b, where the quantized electron and hole energy levels are shown on the envelope of parabolic bands. Therefore, the levels will have effective mass corresponding to the band they occupy. The energy levels are also size dependent as seen
from Equation 2.4. In the strong confinement regime (nanocrystal dimension \( \ll \) excitonic Bohr radius), the electrons and holes can be treated independently, and each is described as a particle in sphere. This can be explained from the fact that the confinement energy scales as \( \frac{1}{a^2} \) while the Coulomb interaction scales as \( \frac{1}{a} \). The Coulomb energy term can be added as a first-order energy correction, \( E_c \). Therefore, using Equation 2.4, the energy of the exciton can be written as follows:

\[
E(n_h, L_h, n_e, L_e) = (E_g)_{\text{bulk}} + \frac{\hbar^2}{2a^2} \left( \frac{\alpha_{n_h,L_h}^2}{m_{h^*}} + \frac{\alpha_{n_e,L_e}^2}{m_{e^*}} \right) - E_c
\]  

(2.7)

The smallest transition is written as \( 1S_h 1S_e \), which corresponds to the transition between...
Figure 2.2: (a) Absorption spectra of PbS nanocrystals with varying radius. (b) Size tuning of excitation energies for various semiconducting nanocrystals. [3]
the highest discrete level in the valence band and the lowest level in the conduction band. The bandgap of the nanocrystal is approximated to this first excitonic transition. The excitonic Bohr radius (EBR) of PbS is $\sim20$ nm and its bulk bandgap is 0.41 eV. Absorption spectra for PbS nanocrystals of radii ranging from $\sim1.3$ to $\sim3.5$ nm are shown in Figure 2.2a, revealing the smallest transition energies in the range of 0.7 (top) to 1.5 eV (bottom). Furthermore, the change in exciton energies for various semiconductors is shown with varying radius of the quantum dots in Figure 2.2b. Note, that the scaling (slope) of exciton energies is different for each semiconductor, which reveals the deviations in dependence of bandgap on $\frac{1}{a^2}$.

2.2.3 Summary

To obtain a complete description of the electronic and optical properties of nanocrystals, the effective mass approach described here can be further complemented with multiband approximations, spin-orbit interactions, multiband mixing and dielectric mismatch [7]. Most of the features resulting from these additions to the existing model are only seen at low temperature. For the purpose of this report, the only important concept needed is that the bandgap for a nanocrystal is dependent on its size, which was perfectly described by the model presented in this section.

2.3 Electron Addition to a Single Nanocrystal

In the previous section, the energy levels of a single nanocrystal quantum dot were defined using the particle-in-a-sphere model and modified Effective Mass Approach. The roadmap for this chapter ends at the description of charge transport for an electron in the nanocrystal solid. To understand the phenomenon of electrical conductivity in any solid, the first question that needs to be answered is, How much energy does it take to add or remove a charge into one of the lattice points of the solid? In this section, the
conditions required for adding electrons to a single nanocrystal are presented.

### 2.3.1 Charging Energy

In a bulk metal, the energy required to add or to remove a charge is equal to the bulk work function. In a molecule, the two energies are nonequivalent and are respectively called the electron affinity and ionization potential. Nanocrystals are somewhere between bulk and molecular-scale materials [21]. The charging energy, also known as Coulomb blockade potential, is then defined as the finite energy cost of adding an electron to a nanocrystal that already has its share of electrons. The origin of charging energy is from the self-capacitance of the nanocrystal quantum dot. The self-capacitance of a particle is defined as the amount of electrical charge that must be added to an isolated conductor to raise its electrical potential by one volt. The reference point for this potential is a theoretical hollow conducting sphere, of infinite radius, centered on the conductor. Using this definition, the self-capacitance of a conducting sphere of radius, $R$ is given by [7]:

$$C_0 = \frac{2\pi \varepsilon_0 R}{\varepsilon_R} \quad \text{(in a semiconductor)}$$

The self-capacitance in a dielectric is schematically illustrated in Figure 2.3. An incoming electron polarizes the molecules creating dipoles. These dipoles orient themselves to create an electric field, which will oppose the one generated by the incoming electron. Therefore, the incoming electron will need to cross this finite energy potential (charging energy) generated by the opposing electric field. Using Equation 2.8, the charging energy is given by:

$$E_c = \frac{e^2}{2C_0} \sim \frac{e^2}{4\pi \varepsilon_0 \varepsilon_R d} \quad (2.9)$$
where $d$ is the diameter of the nanocrystal quantum dot. The capacitance in the above equation is then modified to account for nearest neighbor interactions as follows:

$$E_c = \frac{e^2}{2C_\Sigma} \quad (2.10)$$

$$C_\Sigma = C_0 + C_{nn} \quad (2.11)$$

where the capacitance is the sum of the self-capacitance and nearest neighbor interactions. This has been experimentally observed by Quinn et al. [4] in CoPt$_3$ nanocrystal solids. Figure 2.4 confirms the increase of charging energy in smaller nanocrystals, and also shows the deviation from linear relationship between $E_c$ and $d^{-1}$. The deviation is a direct result of nearest-neighbor interactions.

### 2.3.2 Coulombic Repulsion

The addition of electron also results in Coulombic repulsion between the incoming electron and the electrons already present in the lowest occupied molecular orbital (LUMO).
The Coulombic repulsion energy is denoted as $E_{e-e}$, which is most often ignored due to screening of charges in an environment where the relative permittivity, $\epsilon_r$ is very high.

### 2.3.3 Summary

In summary, there is finite energy cost associated with adding an electron in a single nanocrystal, resulting from the charging energy, $E_c$, and Coulombic repulsion energy, $E_{e-e}$. In a semiconductor nanocrystal quantum dot, the electron also needs to overcome the band gap energy, $E_g$, which is the energy between the highest occupied and lowest unoccupied energy levels. The electron addition energy for adding a first and a second electron is then  [1]:

$$\mu(0/1) = E_g + E_c$$  \hspace{1cm} (2.12)

$$\mu(1/2) = E_g + E_c + E_{e-e}$$  \hspace{1cm} (2.13)
2.4 Nanocrystal Solids

In the previous section, the energy requirements associated with addition of a single electron to a nanocrystal were discussed. In the present section, the concept will be extended to charge transport of electrons in an array of nanocrystals, referred to as nanocrystal solids.

2.4.1 Nanocrystal Superlattice

The arrangement of nanocrystals in a solid is analogous to the concept of lattice points for atoms in conventional semiconducting solids. In both cases, the electrical charge transport is strongly dependent on the order and symmetry of particles, which compose the solid. The driving force for superlattice arrangement has been attributed to maximization of the nanoparticle packing density. Additional contributions from entropic, van der Walls, steric and dipolar forces are also attributed to the formation of a superlattice in nanocrystal thin films. An in-depth review on superlattice formation is provided by Shevchenko and Talapin [30]. The difference in packing order with different processing techniques is shown using high resolution scanning electron microscopy images in Figure 2.5. Note the hexagonal packing of nanocrystals produced by spin-coated films, in

Figure 2.5: High resolution SEM images of PbS nanocrystal solids. (a) drop cast (b) spin coat.
comparison to the structure exhibited by the less ordered films which were drop-casted.

2.5 Electron Transport in Nanocrystal Solids

To better understand charge transport in nanocrystal solids, some of the key concepts, such as the exchange coupling energy and the dispersion in site energies are defined in the following subsections.

2.5.1 Exchange Coupling Energy

The wavefunctions of isolated particles decay exponentially with distance from the particle. However, as the interparticle spacing is decreased, a region of electron density builds up between the particles. The result of this quantum mechanical wavefunction overlap is that overall curvature of the coupled wavefunction is less and so there is a net gain in the kinetic energy of the system. Similarly, the wavefunction of an electron in a particular energy level of a nanocrystal quantum dot can significantly overlap with the corresponding energy level in the neighboring nanocrystal. If the overlap is strong, the two nanocrystals are coupled analogously to the electron in a coupled quantum well or the hydrogen molecule. This net gain in energy is known as the exchange coupling energy and is the major driving force in improving the conductivity of nanocrystal solids. [21]

A coupling system of two adjacent nanocrystals of radius, $R$, with the centers separated by $D$ is shown in Figure 2.6. The exchange coupling energy scales with both size$(2R)$ and separation$(\delta)$ as follows:

$$\beta \sim e^{-\kappa D}$$

(2.14)

where $D = d + \delta$ ($d = 2R$, $\delta =$ interparticle spacing) and $\frac{1}{\kappa}$ corresponds to the length scale for the leaking of the radial Bessel function(from nanocrystal eigenfunction) outside of the quantum dot. This length scale, $\kappa$ is determined from the energy of the highest orbital and the effective mass of electron in that orbital, and is independent of the nanocrystal
radius. The direct consequence of Equation 2.14 is that the coupling strength decreases more rapidly with increasing interparticle spacing for larger quantum dots compared to that of smaller dots. This is shown in Figure 2.7. [5]

2.5.2 Site Energies

Site energy, $\alpha$, corresponds to the absolute energy of the HOMO and LUMO levels in a nanocrystal quantum dot with respect to the vacuum. The size dispersion of nanocrystals is inherent from the synthesis process. It has already been established that the energy levels of a nanocrystal quantum dot vary with the size of the nanocrystals. The dispersion in nanocrystal size translates to dispersion in the site energies, $\Delta \alpha$, of the nanocrystal quantum dots as illustrated in Figure 2.8. The dispersion in site energies is analogous to the defects in conventional crystalline solids. The site energy dispersion will affect the charge transport properties of nanocrystals as an electron moving through the nanocrystal...
solid will interact with the dispersion as if it were defects. [5]

### 2.5.3 The Metal-Insulator (Mott) Transition

Mott insulators are a class of materials that should be conducting based on band theory (for example: tight binding model), but in reality turn out to be insulators. This problem arises from ignoring electron-electron interactions in the band models, which were developed using a single electron model. Similar analysis can be extended to nanocrystal solids, where, if the exchange coupling energy is less than the sum of charging energy and Coulomb repulsive energy (i.e. $\beta < E_c + E_{c-e}$), the solid behaves as a Mott insulator. Collier et al. were able to experimentally demonstrate reversible Mott metal-insulator transition in silver nanocrystal solids. The transition was demonstrated through compression of the silver nanocrystal film, which reduced the interparticle distance and increased the exchange coupling energy. The exchange energy overcomes the Mott insulator tran-
transition and the film becomes metallic as seen in Figure 2.9 [6].

In semiconductor nanocrystals, the Mott transition applies for electrons tunneling between energy levels of adjacent nanocrystals.

2.5.4 Anderson Localization

Anderson Localization was discovered by Phil Anderson, who received a Nobel Prize in 1977 for his investigations. His investigations showed that by increasing the presence of defects, the randomness of crystal deviates from perfectly periodic potential. Eventually, the electron scattering increases to an extent that the electrons will not be able to propagate even in allowed energy bands. His ideas can be extended to nanocrystal solids, where the dispersion in site energy plays the role of defects in Anderson’s theory.
Figure 2.9: Mott metal-insulator transition between 3 and 4. The film becomes metallic at 4 as shown by Second Harmonic Generation signal. [6]

Therefore, if the site dispersion energy is greater than the exchange energy ($\Delta \alpha > \beta$), then Anderson localization will dominate. Remacle et al. show theoretical calculations of Anderson localization for varying dispersion in site energy and interparticle spacing. The results from their simulations demonstrate that, for a highly dispersive system, the interparticle spacing has to be much lower, otherwise charge transport would be localized as seen in Figure 2.10 [7]

### 2.6 Summary

The electron conductivity in a nanocrystal solid falls into either the weak or strong coupling transport regime.

In a weakly coupled system, the interparticle distance between nanocrystals is large, resulting in a lower exchange coupling energy, which cannot overcome the disorder and capacitive charging effect of the system. The charge transport is then dominated by vari-
able range hopping, as the electrons move by sequential tunneling (or hopping) between energy levels of adjacent nanocrystals [31].

In a strongly coupled system, as interparticle separation decreases, the energy states in nanocrystals form bands with an energy width that depends on the exchange coupling energy. At some interparticle separation, the width of the band is sufficient enough for coherent resonant tunneling of electrons to occur between adjacent energy levels, resulting in much improved conductivity.

The defects considered so far were consequences of dispersion in site energies. However, there is another significant source of defect resulting from the trap states, which form due to poorly passivated surface of nanocrystals. The electrons bound in trap states need to be thermally activated to cross the energy barrier determined by the ionization potential of the nanocrystal minus the electron affinity of the organic shell. This type of transport is known as activated hopping.
In reality, the charge transport properties in a nanocrystal solid most likely resembles a combination of the different regimes described in this chapter. In the next two chapters, a characterization tool in the form of field effect transistors is presented to elucidate electronic properties of nanocrystal solids.
Chapter 3

Thin Film Field-Effect Transistors

3.1 Introduction

In addition to the technological interest it generates, the field-effect transistor can also be viewed as a tool for studying charge transport in solid materials [32]. In particular, it gives direct access to the type of free carriers and their corresponding mobility in a semiconductor. In the previous chapter, nanocrystal solids were presented as an exciting new class of materials. There remained, however, a need for the development of a characterization tool to elucidate the electronic properties of these nanocrystal solids. This alone was a significant motivation in fabricating field effect devices, which can be utilized to characterize the charge transport properties of this material system. In this chapter, the operating principles of the field effect transistor are discussed with a focus on fabrication procedures and measurement techniques.

3.2 Operating Principles of a Field-Effect Device

The basic idea of a field-effect transistor is to modulate the current that flows between two ohmic contacts, the source and drain electrodes, by applying a voltage to a third contact, the gate electrode. The device itself is composed of three basic elements: (i)
a semiconducting layer (ii) an insulating layer and the (iii) three electrodes, as shown in Figure 3.1. The source and drain electrodes are in contact with the semiconducting layer, while the gate electrode is isolated by the insulating layer. In the next section, the operating principles of a conventional MOSFET (Metal-Oxide-Semiconductor Field-Effect Transistor) are discussed and then extended for thin film field effect transistors.

### 3.2.1 Operation of a Conventional MOSFET

A MOSFET device behaves similarly to a capacitor; on application of the gate voltage, charges either accumulate or deplete at the semiconductor/insulator interface. The operation of a MOSFET with a p-type semiconductor can be explained by analyzing the energy band diagrams, which are schematically represented in Figure 3.2. The four
Figure 3.2: Energy-band diagram of a p-type MOS structure working in: a) flat-band ($V_g = V_{fb}$); b) accumulation ($V_g < V_{fb}$); c) depletion ($V_g > V_{fb}$) and d) inversion ($V_g > V_t$).

modes of operation of a MOS structure are: Flatband, Accumulation, Depletion, and Inversion.

**Flatband**

At equilibrium, the Fermi levels of the gate metal and the semiconductor align as the charge carriers move towards or away from the semiconductor/insulator interface. A flat-band voltage, $V_{fb}$, which is equal to the workfunction difference between the gate metal and the semiconductor, must be applied to obtain the flat band diagram shown in Figure 3.2a.
Accumulation

If a negative potential is applied to the gate metal, the resulting electric field through the oxide will penetrate the semiconductor, forcing the holes towards the interface. The valence-band edge will move closer to the Fermi level at the insulator-semiconductor interface than in the bulk, which implies that there is accumulation of holes (see Figure 3.2b). Accumulation occurs when one applies a voltage less than the flatband voltage.

Depletion

When a voltage larger than the flatband voltage is applied, the positive charges are depleted from the interface. As a result, the valence band at the interface moves away from the Fermi level of bulk as shown in Figure 3.2c. The depletion layer width increases with increasing gate voltage.

Inversion

Continuing from the depletion mode, as the potential across the semiconductor increases beyond twice the bulk potential, an inversion layer of negative charges is formed at the interface due to the minority carriers as shown in Figure 3.2d. These mobile charges in the inversion layer form a conductive channel at the semiconductor/insulator interface and under a small drain bias will give rise to a field-effect current. The inversion onset voltage is defined as the threshold voltage, \( V_t \).

To summarize, as the gate potential is varied, the MOSFET will operate in one of the four regimes. Correspondingly, the field-effect current in the source-drain channel will modulate with varying gate potential. A conventional MOSFET has an ON state in the inversion regime, which requires the source and drain contacts to be of the same type as the carriers in the inversion channel. Therefore, a MOSFET with a p-type semiconductor substrate is referred to as “n-MOS”, since the source-drain contacts is of n-type in order to inject charges in the inverted conducting channel. A schematic of “n-MOS” field-effect
transistor is shown in Figure 3.3. [33]

### 3.2.2 Thin Film Field-Effect Transistor

The key difference between conventional MOSFET and thin-film field effect transistors is the geometry (Compare Figure 3.3 and Figure 3.1), which results in the conducting channel or the ON state forming in the accumulation mode instead of the inversion mode. The operation in accumulation mode requires the source and drain electrodes to form an ohmic contact with the semiconducting thin film. Therefore, for a p-type semiconductor, a high-work function metal (for example: gold) is generally used as the source and drain electrodes. As a result, the inversion regime is not accessible in the thin film transistors. Therefore, the thin film field-effect transistor only operates in the accumulation and depletion mode. The quality of the thin film transistor is highly dependent on the fabrication of the devices and will be discussed in the subsequent section. [25, 32, 34]

### 3.3 Device Fabrication

The field-effect transistor devices were fabricated on highly doped \(10^{17} cm^{-3}\) n-type silicon wafers with 100nm of thermally grown oxide as the gate dielectric. These wafers...
were purchased from Montco Silicon Technologies. In the following subsections, some of the key issues encountered during the fabrication process will be discussed as deviations from the conventional approach [12] were required to obtain functional devices.

### 3.3.1 First Generation Devices

As mentioned earlier, the highly doped silicon substrate and the thermally grown oxide were respectively used as the gate electrode and insulator. The next step involved the patterning of the source and drain electrodes. The high conductivity and inertness of gold makes it attractive for microelectronic interconnections. However, a thin layer of transition metal such as chromium or titanium needs to be deposited first to enhance adhesion of gold on the silica/silicon substrate. There is a strong correlation between the adhesion properties of the metals and the heat of formation of the oxide, but it has been observed that gold does not form an oxide required for adhesion [35]. Therefore, a thin layer (\(\sim 7\)nm) of chromium was thermally evaporated at the base pressure of \(1 \times 10^{-5}\) torr prior to the deposition of the gold to promote adhesion. This was followed with the DC sputter deposition of a gold film, 40 nm thick at the base pressure of \(5 \times 10^{-6}\) torr and DC power of 100 Watts. The deposition rates for chromium and gold were 0.1 and 0.2 nm/s respectively. The critical fabrication parameters for the source and drain electrodes are the channel width, \(W\), and the channel length, \(L\) as shown in Figure 3.1. A schematic of the mask used to pattern the source/drain electrodes by conventional photolithography [see Appendix B] is shown in Figure 3.4. The varying spacing of interdigitated electrodes in the schematic corresponds to different channel lengths with the smallest and largest spacing of 10 and 100 \(\mu\)m respectively. The device was finished by spin coating the nanocrystal active layer from the solution. This type of architecture is known as bottom-contact device. In the top contact device, the source and drain electrodes are deposited after the deposition of semiconductor film. Although top contact devices are favored, it is difficult to obtain small channel length through shadow masks [36].
Figure 3.4: Schematic and images of field-effect transistor devices. Device pattern and channels are shown from different perspectives.
Figure 3.5: Injection of charge into channel is not direct because of the transition metal wetting layer. As such a non-ohmic contact forms at the interface.
Figure 3.6: Comparison of charge injection between silane and transition metal adhesion devices. The silane device shows superior ohmic contact over the metal wetting layer device.
The first generation devices failed to show any gate modulation and the source-drain electrodes did not form an ohmic contact with the nanocrystal thin film. This effect has been reported in the literature and attributed to the diffusion of transition metal ions along the grain boundaries of gold and forming oxides at the gold surface. The result of this effect is a severe deterioration in the electrical characteristics of gold [37]. Furthermore, the thickness of the conducting channel is estimated to extend only to the first monolayer at the semiconductor/insulator interface, which poses another contact resistance problem as illustrated in Figure 3.5 [38, 39]. Therefore, an alternate method was needed to enhance adhesion of gold without using intermediate transition metal wetting layer. One of the alternate methods was to deposit gold at very high energies for improved adhesion. The gold was sputter deposited at a rate of 0.7 nm/s with DC power of 300 Watts and base pressure of $5 \times 10^{-6}$ torr to enhance adhesion, but this was not entirely reliable as the small features washed away during the photolithography processes. A more reliable solution was found by functionalizing the substrate with self assembled monolayer (SAM). The method for forming this SAM is described in the following subsection.

### 3.3.2 Silanization

Silanization of silicon substrates has been previously reported to improve the adhesion of gold films deposited on silica/silicon [40]. The adhesion efficiency strongly differs according to the deposition procedure. In this section, the procedure for silanizing the silicon substrate, which resulted in high device yields after photolithography, is presented. In the first step, the silicon substrate was cleaned with acetone, isopropyl alcohol and deionized water and heated at $100^\circ C$ for 10 minutes. A clean surface of silica/silicon is hydrophobic. A solution of “Piranha” was then prepared with a three to one ratio of sulfuric acid to hydrogen peroxide. The silicon substrate was treated in the Piranha solution for one hour at $80^\circ C$. The substrate was then rinsed with deionized water
Figure 3.7: Schematic of all the steps involved in forming silane monolayers for gold adhesion.
and dried under brisk flow of nitrogen. It should be noted that the Piranha treatment changes the surface of the substrate from hydrophobic to hydrophilic. The change in surface properties results from the formation of hydroxyl groups on silica. The formation of hydroxyl groups on the surface is essential for the bonding of silane onto silica. After the cleaning and pretreatment, the substrates were silanized by being dipped in the silane solution for a period of more than twelve hours in the glovebox. The silane solution was prepared in the glovebox by mixing 6 mL of 3-mercaptopropyltrimethoxysilane (MPTS) solution in 20 mL of toluene. The thiol functional group in this silane is important because of the strong affinity and binding properties of sulfur with gold. After the silane treatment, the substrate was rinsed with toluene to remove any weakly bonded physisorbed species and dried with nitrogen. The surface became hydrophobic once again after the silane treatment. A thin film of gold was then sputtered onto the silane treated substrate at base pressure of $5 \times 10^{-6}$ torr, DC power of 100 Watts, and deposition rate of 0.2 nm/s. The entire process is illustrated in Figure 3.7. The silanization of substrates significantly improved the adhesion of gold and as a result, the device yield increased to 80%. The devices were checked with an optical microscope after the photolithography process to ensure that all the features were still intact. The gold electrodes on the silane treated samples created an excellent ohmic contact with the nanocrystal solids as seen in Figure 3.6, compared to the best commercially available devices with chromium or titanium as adhesion layers.

The successful devices were then used for field effect measurements, which will be discussed in the following section.

### 3.4 Field-effect measurements

The setup for the field effect measurements is shown in Figure 3.8. The data was controlled and recorded using the Agilent 4155C Semiconductor Parameter Analyzer in a
Figure 3.8: Schematic of measurement setup. Note that the actual sample shown in the inset was scratched to reduce surface area to minimize gate leakage.
Figure 3.9: A sample transfer characteristic of PbS nanocrystal solid thin film field-effect transistor.
Figure 3.10: A sample output characteristic of PbS nanocrystal solid thin film field-effect transistor.
shielded enclosure. All measurements were performed in the dark to avoid any discrepancies from photogenerated carriers. Two types of electrical measurements were performed: transfer characteristics \((I_d - V_g)\) and output characteristics \((I_d - V_d)\). When studying transfer characteristics, the drain voltage is kept constant and \(V_g\) is varied. Alternatively, in order to study the output characteristics, the gate voltage was kept constant while the drain voltage was varied. The grounded electrode is used as reference for both the drain and gate bias and is always considered to be the source electrode by definition. A typical example of the transfer and output characteristics of a nanocrystal solid thin film field-effect transistor is presented in Figure 3.9 and Figure 3.10, respectively.

3.5 Data Analysis: Calculation of Mobility

The calculation of mobility depends on whether the transistor is operated under the linear or saturation regime. The model used to describe the drain current-voltage expression for a field-effect transistor is the Gradual Channel Approximation. The assumptions made with this model is that the electric field lines terminating on the gate are entirely vertical and that the current flow in the channel is entirely horizontal. In the gradual channel approximation, the drain-source current in the channel can be analytically described for linear and saturation regimes as described in the following sections.

3.5.1 Linear Regime

The linear model describes the behavior of a MOSFET biased with a small drain-to-source voltage. The MOSFET can be modeled as a linear resistor whose resistance is modulated by the gate voltage. The general expression for the drain current equals: [25]

\[
I_d = \frac{-Q_{inv}WL}{t_r}
\]  

(3.1)
where $Q$ is the accumulation layer charge per unit area, $W$ is the channel width, $L$ is the channel length and $t_r$ is the transit time. Assuming constant velocity of charge carriers between source and drain, the transit time equals:

$$t_r = \frac{L}{v} \quad (3.2)$$

where the velocity, $v$ is given by:

$$v = \mu \epsilon = \mu \frac{V_{DS}}{L} \quad (3.3)$$

The constant velocity also implies constant electric field and Equation 3.1 can be rewritten as follows:

$$I_d = -\mu Q_{inv} \frac{W}{L} V_{DS} \quad (3.4)$$

It was mentioned earlier that the MOSFET behaves similar to a capacitor and as such the charge density in the channel can described by:

$$Q_{inv} = -C_i (V_{GS} - V_T), \text{ for } V_{GS} > V_T \quad (3.5)$$

Substituting the charge density into Equation 3.4 yields the expression relating the drain current $I_d$ to the applied gate voltage $V_g$ and to the drain voltage $V_d$ for the linear regime:

$$I_d = \mu C_i \frac{W}{L} (V_{gs} - V_t) V_{ds}, \text{ for } (V_{ds} \ll V_{gs} - V_t) \quad (3.6)$$

where $\mu_{lin}$ is the field-effect carrier mobility, $V_t$ is the threshold voltage [32], and $C_i$ is the capacitance per unit area of the insulating layer. The linear model is only valid if $(V_{ds} \ll V_g - V_t)$. This ensures that the velocity, the electric field and the charge density are constant between the drain and the source.

The field-effect mobility can be calculated in the linear regime from the transconduc-
3. Thin Film Field-Effect Transistors

By plotting \( I_d \) versus \( V_{gs} \) at a constant low \( V_{ds} \), with \( V_{ds} \ll (V_{gs} - V_t) \) and equating the value of the slope of this plot to \( g_m \). The calculated values of mobilities for thin nanocrystal solid films will be reported and discussed in the chapter 4.

### 3.5.2 Saturation Regime

When the drain voltage reaches the gate voltage, the voltage between drain and gate approaches zero. This results in the pinch-off of the channel, which causes the saturation of the drain current. For higher values of \( V_d \), after pinch-off has occurred, the saturation regime is described with the same assumptions as the linear model. The key difference here is that due to the large drain-source voltage, the charge in the channel varies between the source and the drain. The expression for the linear model is modified as shown below to account for the differential drop in voltage, \( dV_c \) for differential spacing \( dy \) across the channel.

\[
I_d = \mu C_i \frac{W}{L} (V_g - V_s - V_c - V_t) dV_c
\]  

(3.8)

Both sides can now be integrated with \( y \) varying from 0 to channel length, \( L \), and \( V_c \) varying from 0 to \( V_{ds} \). The drain current is constant, so that the integration results in:

\[
\int_0^L I_d dy = \mu C_i W \int_0^{V_{ds}} (V_g - V_s - V_c - V_t)
\]

(3.9)

The drain current saturation occurs when \( V_{ds} = V_g - V_t \), which is substituted in Equation 3.9 to give the following expression for saturated drain current:

\[
I_d = \mu_{sat} C_i \frac{W}{L} \frac{(V_{gs} - V_t)^2}{2}, \text{ for } V_{ds} > V_{gs} - V_t
\]  

(3.10)
In the saturation regime, $\mu_{\text{sat}}$ can be calculated from the slope of the plot of $\sqrt{I_d}$ versus $V_g$. It is important to note that the $W/L$ ratio must be at least 10 in order to minimize the effects of fringe currents flowing outside the channel on the calculated mobility value; otherwise this value is overestimated [25].

### 3.6 Conclusions

The operating principles of metal-oxide-semiconductor field-effect transistors were presented and the model was extended to describe thin film field-effect transistors. This was then followed with guidelines for the fabrication of a thin film field-effect transistor device. It was discovered that the transition metal wetting layer used to improve adhesion of gold on silica failed to produce working devices. The fabrication process was then modified by functionalizing the silica/silicon substrate with self-assembled monolayers to improve the adhesion of gold. The adjustment in the fabrication procedure resulted in very high quality thin film field-effect transistors, which were capable of probing semiconducting nanocrystal solids with poor transport properties. Finally, a procedure for measurements and data analysis was presented to extract mobility and doping type from these devices. In the following chapter, the thin film field-effect transistors will be showcased for the characterization and engineering of nanocrystal solids.
Chapter 4

Engineering Nanocrystal Solids

4.1 Introduction

The previous chapter discussed the operating principles and fabrication techniques of a field-effect transistor. In addition, techniques for measurement and data analysis were presented to extract mobility of a semiconductor film from the field-effect device. The present chapter reports changes in doping level and charge transport properties of PbS and PbSe nanocrystal solids with chemical and heat treatments. The field-effect measurements were utilized to characterize the evolution of the aforementioned properties. Furthermore, these measurements were used to understand the increases in power conversion efficiencies of PbS and PbSe nanocrystal solid based photovoltaic devices.

4.2 Engineering PbSe Nanocrystal Solids

4.2.1 Sample Preparation

The synthesis and ligand exchange of PbSe nanocrystals were carried out respectively by L. Levina and G Koleilat. The synthesis and exchange procedure will be described elsewhere [41]. The exchanged PbSe nanocrystals were diluted to a concentration of 10
mg/mL and spin-coated on to the field effect devices. The nanocrystal solution vials were sealed and stored in the glovebox. The thickness of the film was measured to be 50 nm. Note that all film thickness measurements described in this report were determined using a calibrated Veeco Dimension 3100 Multimode atomic force microscope in tapping mode. The field effect measurements were then obtained as described in the previous chapter. The change in absorption of the film was characterized on a Cary 500 UV-Vis-IR photospectrometer.

4.2.2 Treatment - Modification of PbSe nanocrystal solids

The nanocrystal films deposited on the field-effect devices were immersed in a freshly-prepared 1 mM solution of 1,4-benzenedithiol (BDT) in anhydrous acetonitrile. The devices were treated for 10 minutes in the solution and then vacuum dried for 30 minutes in the antechamber of the glovebox. The field-effect and absorption measurements were repeated again on the same sample after the treatment.

4.2.3 Results: Evolution of Charge Transport Parameters with Treatment

The evolution of conductivity, mobility and doping of the PbSe nanocrystal solid with benzenedithiol treatment is presented in the following subsections.

Conductivity

The conductivity of the PbSe nanocrystal solid increased from $1.35 \times 10^{-5} \, S \, cm^{-1}$ to $2.35 \times 10^{-5} \, S \, cm^{-1}$ after treatment with benzenedithiol. The dimensions of the film: $L = 10 \, \mu m$, $W = 3 \, mm$, $d = 50 \, nm$ were substituted in the following equation to extract conductivity from the conductance, $G$. The conductance was obtained from the slope of
Figure 4.1: Change in conductivity of PbSe nanocrystal solid after benzenedithiol treatment.
Figure 4.2: Transfer characteristics for PbSe nanocrystal solids before treatment.

I-V graph shown in Figure 4.1 at zero gate bias.

\[ \sigma = \frac{L G}{dW} \]  

(4.1)

The conductivity of the film is also related to carrier concentration and mobility as follows:

\[ \sigma = n e \mu \]  

(4.2)

An increase in conductivity directly relates to increase in either mobility or carrier concentration or both.

**Mobility**

The transfer characteristics for before and after-treated PbSe nanocrystal solids are respectively shown in Figure 4.2 and Figure 4.3. The mobility in the linear regime is calculated from the slope of the transfer curves as described in the previous chapter. The linear mobility of the nanocrystal solid increased from \(7.2 \times 10^{-6} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for
the untreated PbSe nanocrystals to $1.1 \times 10^{-4} cm^2 V^{-1} s^{-1}$ after treatment. The transfer characteristics for both before and after treatment showed that as the applied gate voltage became more negative, the drain-source current increased in magnitude. This is the characteristic of a p-type field-effect transistor operation, indicating a p-type doping of the PbSe nanocrystal solid.

**Doping**

The conductivity and mobility values were utilized to calculate the hole carrier concentration in PbSe nanocrystal solid using equation 4.2. The hole carrier concentration decreased by ten times from $1.2 \times 10^{19} cm^{-3}$ to $1.4 \times 10^{18} cm^{-3}$ after treatment.
4.2.4 Discussions: Evolution of Charge Transport Parameters with Treatment

The simultaneous tuning of both the doping level and mobility of the PbSe nanocrystal solid with benzenedithiol treatment is shown in Figure 4.4. In the following subsections, some of the physics behind the chemical treatments will be discussed.

Mobility

The increase in mobility is directly attributed to the increase in exchange coupling energy, $\beta$, between the nanocrystals in the solid. The exchange coupling energy decreases exponentially with increasing spacing between adjacent nanocrystals as seen in chapter 2. When the PbSe nanocrystal solid is treated with benzenedithiol, the interparticle spacing of the solid decreases as the longer octylamine ligands ($1.2\text{nm}$) are replaced with shorter benzenedithiol ligands ($0.7\text{nm}$). Furthermore, the benzenedithiol linker has functional groups on both ends which can effectively crosslink the solid by binding with two adjacent nanocrystals. The benzenedithiol also passivates the nanocrystal by saturating
the surface dangling bonds that trap carriers in mid-gap states [12]. The passivation study of nanocrystal solids with benzenedithiol treatment is described in chapter 5. The decrease in interparticle spacing and increase in exchange coupling energy was verified with absorption measurements. The absorption peak of the nanocrystal solid was red shifted after the treatment, which indicates a decrease in bandgap towards more bulk like characteristics and greater exchange coupling [42]. The dielectric constants of octylamine and benzenedithiol are approximately similar and as such should not have a significant effect on the charging energy. The dispersion in site energy depends on the nanocrystal synthesis parameters and stays constant before and after the treatment as seen in the absorption measurements. Site dispersion energy and charging energy is defined in chapter 2. Electrical conduction through molecules depends critically on the delocalization of the molecular electronic orbitals and their connection to the metallic surfaces. Thiolated molecules (-SH) have excellent binding properties to metals such as gold and lead. Benzenedithiol is an aromatic molecule and has ring of delocalized electrons and as such proves to be one of the highly effective molecular conductor [43]. Previous report
has also shown coherent electron transfer between adjacent nanocrystals crosslinked with benzenedithiol [42]. In conclusion, the benzenedithiol treatment increases mobility of the PbSe nanocrystal solid by decreasing the interparticle spacing and proving to be better molecular conductor.

**Doping Level**

The hole carrier concentration in PbSe nanocrystal solid decreased almost ten times after the treatment, rendering the solid less p-type. The initial p-type doping of the PbSe nanocrystal solid has been correlated with oxidation of the nanocrystals in the ambient atmosphere [12]. PbSe nanocrystal solids were recently shown to be doped n-type through the use of hydrazine. The solids were then switched to p-type by vacuum treatment or low temperature heating (100°C), which served to remove the hydrazine from the film. It is believed that the removal of hydrazine renders the PbSe surface accessible for oxidation, which results in net p-type doping [12]. If oxidation results in p-type doping, then the treatment with benzenedithiol must remove some of this oxidation to explain the reduction in hole carrier concentration.

**4.2.5 Photovoltaic Response of PbSe nanocrystal solid**

The PbSe nanocrystal solids were utilized to fabricate a photovoltaic device. The nanocrystals were spin-coated onto an ITO(Indium Tin Oxide) substrate and then a top contact of Magnesium metal was evaporated. There was no photovoltaic response observed for the untreated PbSe nanocrystal solids. After treatment with benzenedithiol, the photovoltaic response of the device significantly improved. The power conversion efficiency of the device was reported to be greater than 1% [41]. The photovoltaic devices were fabricated and measured by G. Koleilat.
4.3 Engineering PbS Nanocrystal Solids

In the previous section, the engineering of doping level and mobility of PbSe nanocrystals solids were presented. In the present section, the evolution of electronic properties for PbS nanocrystal solids will be studied.

4.3.1 Sample Preparation

The synthesis of PbS nanocrystals were carried out by L. Levina. The as-synthesized nanocrystals were passivated with oleic acid ligands. These ligands were replaced in solution with more volatile and shorter butylamine ligands using the exchange procedure described in Appendix A. The exchanged PbS nanocrystals were diluted to a concentration of 10 mg/mL and spin-coated on to the field effect devices. The nanocrystal solution vials were sealed and stored in the glovebox. The thickness of the film was measured to be 40 nm.

4.3.2 Treatment - Modification of PbS nanocrystal solids

The nanocrystal films deposited on the field effect devices were immersed in a freshly-prepared 4% by volume solution of ethanedithiol (EDT) in anhydrous acetonitrile. The devices were treated for 10 minutes in the solution and then annealed at 90°C for 2 minutes. Field-effect measurements were taken before any treatments, after ethanedithiol treatment, and finally after annealing on the same sample. The evolution of charge transport parameters in PbS nanocrystal solid with treatments is presented in the subsequent section.
Figure 4.6: Transfer characteristics for PbS nanocrystal solids before treatment. The drain-source current increases with negative gate potential, which is a characteristic of p-type FET operation.

Figure 4.7: Transfer characteristics for PbS nanocrystal solids after ethanedithiol treatment. The instability in the measurement corresponds to the rapid oxidation after ethanedithiol treatment.
Figure 4.8: Transfer characteristics for PbSe nanocrystal solids after ethanedithiol treatment and annealed in air.

Figure 4.9: Evolution of charge transport parameters of PbS nanocrystal solid with treatments.
<table>
<thead>
<tr>
<th></th>
<th>Doping Level ($cm^{-3}$)</th>
<th>Mobility ($cm^2V^{-1}s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>$3.2 \times 10^{18}$</td>
<td>$3.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>EDT</td>
<td>$2.4 \times 10^{18}$</td>
<td>$1.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>EDT+Air Annealed</td>
<td>$7.2 \times 10^{18}$</td>
<td>$1.9 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 4.1: Charge carrier mobility and concentration calculated from field-effect measurements for untreated, ethanedithiol treated and air-annealed PbS nanocrystals.

4.3.3 Results: Evolution of Charge Transport Parameters with Treatment

The charge carrier concentration (doping level) and charge carrier mobility were calculated using the same procedure described for PbSe nanocrystal solids earlier. These values are tabulated in Table 4.1. The field-effect transfer characteristics for before and after treatments on the same device are shown in Figures 4.6, 4.7, and 4.8. The transfer characteristics show p-type operation for all cases. The evolution of charge transport parameters normalized to untreated case is shown in Figure 4.9.

4.3.4 Discussions: Evolution of Charge Transport Parameters with Treatment

The increase in mobility of PbS nanocrystal solid after ethanedithiol treatment was attributed to improved exchange coupling. The improvement is a result of decreased interparticle spacing due to cross-linking of nanocrystals with shorter ethanedithiol linkers. Moreover, the ethanedithiol treatment removed existing surface oxide on the PbS nanocrystal solids. X-ray photoelectron spectroscopy was utilized to examine the oxidation state of PbS nanocrystal solids with treatment. It was observed that treatment with ethanedithiol removed PbO content, which was then reestablished after annealing in air. The spectroscopy results were obtained by E. Klem and are presented elsewhere [44]. In PbS, PbO produces net p-doping as oxygen is effective in the formation of $D^-\,$ acceptor states [45, 46]. Furthermore, previous reports have shown p-type doping of bulk PbS by
annealing in air [47, 48]. Therefore, the removal of native surface oxide with ethanedithiol treatment resulted in a net reduction of doping level. The nanocrystals were then re-oxidized with controlled annealing in air to increase the doping level to almost twice as much from the original untreated nanocrystal solid.

4.3.5 Photovoltaic Response of the PbS nanocrystal solid

Photovoltaic devices offer an ideal opportunity to demonstrate the effect of engineering doping and mobility of nanocrystal solids. Photovoltaic devices were fabricated on porous ITO electrode infiltrated with ethanedithiol cross-linked PbS nanocrystals and then completed by a top Mg contact. Electrons escape into the Mg while holes travel to the ITO. The power conversion efficiency of this device was increased from 0.4% to 2% after annealing in air. The increase in efficiency was attributed to increase in $V_{oc}$ of the photovoltaic device. The $V_{oc}$ is related to the offset between the semiconductor Fermi level and the Mg contact work function. The offset increase resulted from more p-type doping of the nanocrystal solid. The photovoltaic devices were fabricated and measured by E. Klem. [44]

4.4 Field Effect Mobility

4.4.1 Local Mobility versus Field-Effect Mobility

The transport characteristics in nanocrystal solids are not well defined. In chapter 2, two possible types of transport mechanisms were considered for charge carriers in nanocrystal solids. If the nanocrystals in the solid are strongly coupled, the charge transport would be similar to that of a conventional crystalline semiconductor. In this case, the field effect mobility would closely represent that of the entire system. However, in the case of weak coupling between nanocrystals, the charge transport could follow the variable range hopping model. The transport properties in a weakly coupled system is dominated
by localized states [49]. As such, on application of high gate voltage, the charge carriers will accumulate in the semiconductor close to the insulator. They will fill all the trap states and the additional charges will see enhanced mobility. In conventional field effect transistors, the calculation of mobility as described in chapter 3 does not take into account the distribution of charges in the accumulation layer. The charge distribution is in fact not uniform and decreases away from semiconductor/insulator interface into the bulk. The consequence of this is that not all charge carriers will have the same mobility and those that are closer to the interface will have higher mobility than in the bulk. In the present chapter, the calculations of mobilities in nanocrystal solids were utilized to understand charge transport in devices. The question that needs to be asked is how accurate does the field effect mobility describe the transport in nanocrystal solids? To answer the question, the distribution of charge carrier density in the accumulation channel needs to be calculated. These calculations are beyond the scope of this report, but a detailed study by Tanase and coworkers [50] demonstrates that in spite of strong variations in the local mobility, the conventional field-effect mobility is a relatively good estimate for the mobility of charge carriers in the case of disordered system. Furthermore, the treatments were followed on the same device and the measurements were kept consistent to ensure that the relative changes can be easily compared, even if the absolute mobilities might not be exact. [51–53]

4.4.2 High Off-State Leakage Current

The field effect devices presented in this chapter suffered from very low $I_{on}/I_{off}$ ratio (ie weak modulation). The low $I_{on}/I_{off}$ ratio is a consequence of high leakage current in the off-state (depletion mode). The leakage current issue is inherent in the thin film transistor architecture. In the conventional MOSFETs, the drain-source current is blocked by $n^+\text{-p}$ junction, but in the thin film-field effect architecture, the source and drain form ohmic contacts. The schematic of leakage pathway is shown in Figure 4.10. Therefore, although
high mobility is necessary for high current output in "on" state, a low conductivity is required to ensure low off-state current. In conclusion, because of the high doping density in PbS and PbSe nanocrystal solids, there is significant drain-source current observed in the off-state. [8]

4.5 Conclusions

This chapter presented different routes to engineering the mobility and doping level of nanocrystal solids. The main achievements outlined include:

- The mobility and doping level of PbSe nanocrystal solids were reported and then engineered with benzenedithiol treatment.

- The evolution of charge transport parameters with treatment was followed with field-effect measurements.

- The engineered films were utilized in fabricating photovoltaic devices with power conversion efficiencies of 1%.
• A different engineering route was then shown for PbS nanocrystal solids. Ethanedithiol treatment of PbS solids showed a ten times increase in mobility. Controlled oxidation was then employed to increase the charge carrier density in the solid.

• The engineering of mobility and carrier concentration in the PbS nanocrystal solids resulted in five times increase in power conversion efficiency of up to 2% in photovoltaic devices.

This chapter showcased the effectiveness of engineering nanocrystal solids. In the next chapter, these nanocrystal solids will be utilized as building blocks for fabricating an all nanocrystal heterostructure.
Chapter 5

Nanocrystal Heterostructures

5.1 Introduction

The previous chapter demonstrated the engineering and characterization of the transport properties for nanocrystal solids. In the present chapter, the nanocrystal solids are utilized as building blocks for fabricating an all-nanocrystal based heterostructure. The heterostructure was fabricated with nanocrystals of different bandgaps to obtain confinement of electrons and holes in the active layer. The resulting structure was then utilized to demonstrate solution processed electroluminescent device with an estimated efficiency of 0.5% at peak wavelength of 1.58 \( \mu m \) in the telecommunications regime. Note that the ideas, measurements, and experimental setups discussed in this chapter were developed in significant collaboration with Dr. S. Hoogland.

5.2 Fabrication and Characterization

5.2.1 Layer-by-layer

The layer-by-layer deposition technique has been previously reported in fabrication of self-assembled monolayers of metal nanoparticles [54]. Recently, colloidal semiconductor
nanocrystals have also been linked this way to form 3-D nanocrystal solids [42, 55]. In this section, the layer-by-layer deposition technique will be briefly described:

**Deposition**

For Indium-Tin-Oxide (ITO) coated substrate, the ITO surface was first functionalized with the 3-mercaptopropytrimethoxysilane molecules as described in chapter 3. The gold coated substrates were functionalized with dithiol (HS-R-SH) molecules as sulfur binds very strongly with gold. Thereafter, the functionalized substrates were immersed in the PbS nanocrystal solution to form the first monolayer. Following the self-assembly of the first monolayer, the ligands of this monolayer were further modified with dithiol molecules, which form covalent bonds between the nanocrystals and one thiol end group. The remaining thiol end groups of these linker molecules are left free for assembling the next nanocrystal layer. The ligand modification was performed by immersing the sample in dithiol solution. By repeated alternate immersion in the nanocrystal and thiol solutions, multilayer devices were fabricated. Each layer is independent of the other during deposition, and thus a variety of multilayer configurations were achieved by simply changing the nanocrystal solutions.

**Characterization**

Exchanged PbS nanocrystals with butylamine ligands were dissolved in toluene solution with concentration of 5mg/mL. The linkers, 1,4-benzenedithiol and ethanedithiol were also prepared in toluene solution with 1mM and 4% by volume concentration respectively. The substrates were rinsed with toluene after every immersion to remove weakly bonded physisorbed species of nanocrystals or linkers. The characterization of devices fabricated utilizing this layer-by-layer self-assembly technique will be presented in this section.

The evolution of absorption for the nanocrystal film with increasing monolayers is shown respectively for both benzenedithiol and ethanedithiol linkers in Figure 5.1 and
Figure 5.1: Increase in absorption with layer-by-layer formation of PbS nanocrystal monolayers linked with benzenedithiol.

Figure 5.2: Increase in absorption with layer-by-layer formation of PbS nanocrystal monolayers linked with ethanedithiol.
Figure 5.3: Comparison between ethanedithiol and benzenedithiol linked monolayer quality. The linear increase for ethanedithiol shows better packing fraction and monolayer quality.

Figure 5.4: Shift in absorption after treatment. A higher red shift indicates higher packing and increased exchange overlap between neighboring nanocrystals.
Figure 5.2. It was observed, that monolayers failed to form with longer oleic-acid capped nanocrystals due to steric effects. Therefore, the passivating ligands of nanocrystals have to be of the same size as the linker molecules. The absorption intensity versus the number of layers is plotted in Figure 5.3. The intensity is plotted in log scale because absorption is exponentially related with the thickness of the film. The nonlinearity in absorption increase for benzenedithiol is result of poor/incomplete monolayer formation compared to ethanedithiol linkers. The absorption peak of PbS nanocrystal solids fabricated with ethanedithiol linker is red shifted compared to those fabricated with benzenedithiol linkers as shown in Figure 5.4. This suggests greater exchange coupling and packing for ethanedithiol linked nanocrystals.

Summary

The nanocrystal solids fabricated utilizing the layer-by-layer technique show excellent control in tuning of thickness and individual monolayers. However, all the devices made from this technique were shorted when a top-metal contact was deposited. This was a direct consequence of the high porosity of these films, which is evident in the scanning electron microscopy image shown in Figure 5.5.

5.2.2 Spin Coating

Spin-coating has widely been used as a deposition method due to its ability to form uniform films over large area and its applicability in large-scale production [56]. The inherent problem with utilizing spin-coating for building stacked nanocrystal solid heterostructure is that the first layer dissolves back during the deposition of the second layer. Therefore, the first layer had to be immobilized. It was observed that if the films were treated with bidentate linkers, such as dithiols, the nanocrystals in the solid would cross-link with each other. After such treatment, the film neither dissolved nor swelled on re-exposure to nonpolar solvents. Immobilizing the film provided with a quick and
Figure 5.5: A scanning electron microscopy image of benzenedithiol linked layer-by-layer nanocrystal solid.
highly efficient route in fabricating heterostructures from stacked nanocrystal solids.

The thickness of each layer was controlled by varying the concentration of nanocrystal solution and the spin-speed of the spin-coater. The benzenedithiol was utilized as the bidentate linker for cross-linking the nanocrystal solids. The films were immersed in benzenedithiol solution for 20 minutes. After treatment, the films were washed with acetonitrile to remove any loosely bounded physisorbed species. Alternate spin-coating and treatment was used to fabricate stacked nanocrystal heterostructure. Since each layer is independently spin-coated, different stacking structure can be realized by simply changing the nanocrystal solution.
Characterization

The scanning electron microscopy images of the nanocrystal solid after treatment with benzenedithiol is presented in Figure 5.6. The film shows some evidence of cracking because of the cross-linking of nanocrystals resulting in reduced interparticle spacing. The cracks were effectively filled by spin-coating a second more dilute layer of the same nanocrystals. Through careful optimization of nanocrystal concentration and spin parameters, the surface roughness and film thickness can be controlled down to few monolayers.

Summary

The process described here has been previously reported in principle for fabricating stacked nanocrystal heterostructure, but has never been demonstrated [12]. A scanning microscopy image of stacked nanocrystal heterostructure is shown in Figure 5.6. The possibilities leading from here are endless as one could envision a tandem solar cell type architecture to a p-n junction device. The elegance of this method is that it is entirely solution processable and as such highly cost-effective compared to epitaxially grown heterostructures. There are also countless degree of freedoms, which can be employed in the tuning of each layer through treatments and size variation. In the next section, an example of type-I heterostructure will be demonstrated.

5.3 Nanocrystal Heterostructures for Electroluminescent Device

The performance of an electroluminescent device is strongly related with efficient carrier confinement in the active layer and the internal radiative recombination efficiency of the active layer. The carrier confinement was achieved through the heterostructure architecture. The internal recombination efficiency, also known as the photoluminescence
quantum efficiency (PLQE) was increased with benzenedithiol treatment as described in
the following sections.

5.3.1 Photoluminescence Quantum Efficiency (PLQE)

PLQE is defined as the ratio of the photons emitted from the nanocrystals over the
number of the absorbed exciting photons. It depends on surface states, defects in the
 crystal lattice, and the energy transfer among nanocrystals. Previous efforts in the group
have resulted in optimization of PLQE for PbS nanocrystals in solution. While the PLQE
for PbS nanocrystals in solution is 50%, it severely decreases to less than 0.3% in thin
films of PbS nanocrystal solids. A PLQE of 5% has been reported for nanocrystal/MEH-
PPV(polymer) composite film, but to date there have been no improvements reported in
PLQE for nanocrystal solids. [57]

The low PLQE in the thin film is a result of energy transfer to non-luminescing
nanocrystals and charge separation due to wavefunction overlap between neighboring
nanocrystals. To elaborate this concept further, consider the formation of an exciton
in a nanocrystal. An exciton is a quasi-particle that forms when Coulomb-interacting
electrons and holes in semiconductors are bound into pair states. The exciton formation
in nanocrystal could be either through optical excitation or electrical injection. In optical
excitation, the electron from the valence band of nanocrystal is excited to the conduc-
tion band forming an electron-hole pair; whereas in electrical injection, the exciton is
formed by injecting both an electron and a hole into the nanocrystal. When the excitons
recombine, the energy is released in the form of radiation. The radiation is referred to
as either photo- or electroluminescence respectively, depending on whether the excitons
were formed optically or through electrical injection. In solution, the excitons have no
means to transfer to the neighboring nanocrystals and as a result the radiative efficiency
is only governed by lattice defects within the nanocrystal. However, in thin films, due to
exchange coupling, the excitons can transfer between neighboring nanocrystals and can
Table 5.1: Photoluminescence Quantum Efficiency (PLQE) changes with chemical treatments on PbS nanocrystals.

Plasticity become trapped in long lived (> 1µs) surface states. To remove long-lived trap states, the dangling surface bonds (surface atoms missing ligands) on nanocrystals need to be passivated. This can be accomplished by treatment of solid with ligand possessing an end functional group that would bind very strongly to the surface of nanocrystal.

The details of experiment setup and calculation of PLQE are presented elsewhere [57], but in essence, the PLQE is calculated by taking the ratio of photoluminescence power output over the absorbed laser power input. The PLQE changes for as-synthesized (oleic-acid capped) and exchanged (butylamine capped) PbS nanocrystal solids with treatments are tabulated in table 5.1. The increase in PLQE with benzenedithiol treatment has been attributed to improved passivation of surface trap states. The sulfur endgroup in thiol binds strongly with the Pb cation, and in process removes electron traps from unpassivated PbS nanocrystals. It is interesting to note that treatment with ethanedithiol reduces PLQE of the film. Ethanedithiol is a smaller molecule than benzenedithiol and forms more tightly packed films. As a result, the energy transfer from smaller to bigger nanocrystals is increased, causing a reduction on the overall efficiency due to nonradiative deactivation on surface states upon exciton transfer to an adjacent nanocrystal [58].
Figure 5.7: The absorption spectrum of the nanocrystals utilized to fabricate the electroluminescence device.

### 5.3.2 Device Fabrication

Several possible heterostructures were tried, but for the sake of brevity, the heterostructure that gave the best efficiency will be presented in this section. The oleic acid capped PbS nanocrystals were exchanged with shorter butylamine ligands [see appendix A]. The exchanged PbS nanocrystals were dispersed in chloroform solution at the concentration of 20 mg/mL. The devices were fabricated on conductive, yet transparent Indium-tin-oxide (ITO)-coated glass substrates. The fabrication steps are described sequentially below:

1. PbS nanocrystals with absorption peak at 1.1 $\mu$m were spin-coated onto the ITO substrate. The thickness of the film as measured with AFM was 80 nm.
2. The film was treated with 0.5 mM 1,4-benzenedithiol/acetonitrile solution for 20 minutes. The device was washed with toluene after treatment to remove weakly absorbed species.

3. Once benzenedithiol treated, the films became insoluble, which allowed for the deposition of the next layer.

4. PbS nanocrystals with absorption peak at 1.45 $\mu$m were spin-coated on the previously deposited 1.1um film. The thickness of this film was 80 nm, bringing the total thickness of the device to approximately 160 nm.

5. The device was immersed again in the benzenedithiol solution as described in step 2.

6. The device was then loaded into the evaporation chamber where an ultra-thin layer (2 nm) of LiF was thermally evaporated at the pressure of $2 \times 10^{-5}$ torr and a deposition rate of 0.1 nm/s. A shadow mask was utilized to deposit top contacts of 300 $\mu$m in diameter.

7. Following the deposition of LiF, more than 100 nm of aluminium was thermally evaporated at pressure of $2 \times 10^{-5}$ torr and deposition rate of greater than 2 nm/s.

The absorption spectra for both sets of nanocrystals are shown in Figure 5.7.

5.3.3 Experimental Setup and Measurement Procedures

The current-voltage scans were obtained using Keithley 2400 source meter. The electro-luminescence spectrum was obtained with an Ocean Optics NIR512 near-infrared spectrometer. The optical power output was measured with a near-infrared InGaAs Newport power meter (model 918-IG). The light emitted from the device was considered to be a point source, which was collected by a 500 $\mu$m core optical fiber at a distance of $\sim 2.5$ mm away from the source.
5.3.4 Results and Discussions

The optical and electrical power measurements are shown in Figure 5.9. The external electroluminescence quantum efficiency (ELQE) $\eta_{ext}$, is defined as the ratio of photons emitted from the device to the number of carriers injected into the device:

$$\eta_{ext} = \frac{\text{Photons Out}}{\text{Electrons In}} = \frac{P_{out}/h\nu}{I_{in}/q}$$

(5.1)

The light extracted from the device was assumed to follow a lambertian distribution [59] and as such the optical power output was modified with a correction factor of 100. The ELQE was then calculated using equation 5.1 to be $\sim0.5\%$. The device architecture along with proposed bandgap alignment is shown in Figure 5.8. In this device, the elec-
Figure 5.9: The optical and electrical power output from the EL device.
Figure 5.10: The electroluminescence and photoluminescence spectra of the EL device. The EL spectrum correlates very well with the PL spectrum.
Figure 5.11: Leakage of confinement shown as emission from the non-active layer becomes visible in the EL spectrum.
Electrons are injected from aluminum, while holes are injected from ITO. Lithium fluoride was used as the dielectric barrier. When an ultra-thin layer of LiF is backed by an aluminum metal layer, the system behaves as an efficient electron injector [60]. The heterostructure is needed for the confinement of electrons and holes in the active layer of 1.45 $\mu$m nanocrystal solid. The electrons injected in the 1.45 $\mu$m nanocrystal solid are blocked by higher bandgap 1.1 $\mu$m nanocrystal solid. The electroluminescent spectrum presented in Figure 5.10 shows no emission from 1.1 $\mu$m layer, which proves efficient carrier confinement. Furthermore, the electroluminescence spectrum corresponds well with the photoluminescence spectrum of the 1.45 $\mu$m nanocrystal solid. The peak wavelength (1.58 $\mu$m) of the electroluminescence spectrum differs from the absorption peak (1.45 $\mu$m) due to Stokes shift. Reducing the film thickness of the 1.45 $\mu$m active layer from 80 nm to 20 nm, resulted in a weaker confinement of carriers and an additional emission from 1.1 $\mu$m layer was observed as shown in Figure 5.11.

5.4 Conclusions

In this chapter, a general approach to fabrication of nanocrystal heterostructure from nanocrystal solids was presented. An electroluminescent device was then fabricated utilizing the nanocrystal heterostructure. The external quantum efficiency of this device was calculated to be 0.5 % with the peak emission in the infrared communication wavelength at 1.58 $\mu$m.
Chapter 6

Conclusions

6.1 Contributions to the field

Traditional solids present limited capabilities for bottom-up materials engineering. Atoms that make solids are to all purpose immutable. Therefore, artificial atoms, for example nanocrystals, are required to fabricate designer materials with specific properties. The nanocrystals can be assembled into a solid, and in doing so gives access to more parameters for engineering structural, electrical and optical properties. Aside from the technological interest, these nanocrystal solids are excellent model systems for the investigation of the fundamental physics of solids. In particular, the notion that the site energy, coupling strength and the lattice dimensionality and order can be varied and characterized is very powerful. Therefore, the study of these nanocrystal solids offers potential for making a significant impact in the field of solid state physics.

If nanocrystals were building blocks for nanocrystal solids, then by analogy, the nanocrystal solids are the building blocks for nanocrystal heterostructures. Prior to this work, solution processed heterostructures with nanocrystals were only fabricated in conjunction with organic polymers. In this work, the very first all nanocrystal heterostructure is demonstrated. Furthermore, this heterostructure is utilized to fabricate
never reported solution processed electroluminescent devices with an emission in the communication wavelength of 1.58 µm.

### 6.2 Thesis Summary

In the introductory chapter, the six main questions this thesis aimed to resolve were listed. As a summary, they are repeated here with the corresponding answers:

1. **How does an electron move in a nanocrystal solid?**

   In chapter 2, the charge transport theory of an electron in a nanocrystal solid was described. Instead of utilizing dense computer simulations, traditional concepts from condensed matter physics were applied to obtain analytical solutions. First, the size dependency of the bandgap in a nanocrystal was explained through combination of the particle in a sphere model and the effective mass approach. The nanocrystal was then used as the building block to form an “artificial” solid. The transport of electrons in this “artificial” solid was linked primarily to the exchange coupling between nanocrystals. If the interparticle spacing between the nanocrystals is sufficiently large for a strong overlap of electron wavefunctions between adjacent energy levels, then electrons can tunnel resonantly between the nanocrystals. However, for the case of weakly coupled system, the electrons tunnel sequentially to nearest neighbors through variable range hopping. The conductivity in this type of sequential tunneling is highly dependent on temperature. In conclusion, to improve electron conductivity within the nanocrystal solids, the interparticle spacing has to be reduced to improve exchange coupling.

2. **What are the key charge transport parameters for a nanocrystal solid?**

   Charge carrier density and charge carrier mobility are the two key charge transport parameters described in this report. The charge carrier mobility is an overall mea-
sure of the efficiency of charge transport in any conducting material. The charge carrier density reveals the doping level and the type of majority charge carrier (electron or hole) in a semiconducting solid.

3. How can these charge transport parameters be reliably characterized?

Field-effect transistors were utilized in characterizing the charge transport parameters identified in the previous answer. The operating principles of a field-effect transistor were described in chapter 3. The nanocrystal solids are not optimized for field-effect transistor measurements and in most cases the mobility was also very low. Therefore, a high performance fabrication route was developed to measure the charge transport characteristics of nanocrystal solids. This fabrication process included the use of a self-assembled monolayer of silane molecules on the silica/silicon substrate to improve the adhesion of gold.

4. How to engineer charge transport parameters of PbS and PbSe nanocrystal solids?

As shown in chapter 4, the PbS and PbSe nanocrystal solids were engineered with chemical treatments. The PbSe nanocrystal solids were immersed in a chemical solution of benzenedithiol and the evolution of charge transport parameters was observed with field effect measurements. The mobility of the PbSe solid increased by up to 15 times from its initial value after the treatment. The doping level decreased by ten times. The engineered films were utilized to fabricate photovoltaic devices of power conversion efficiency greater than 1%. For PbS nanocrystal solids, the doping level was controlled through oxidation of the nanocrystals. First, the native oxide was removed with an ethanedithiol treatment, which also resulted in a ten times increase in mobility due to decreased interparticle spacing. The solids were then modified with controlled oxidation through annealing in air. The overall effect of oxidation was to increase the doping level of the solids. The photovoltaic devices engineered with these treatments resulted in a significant improvement in
the power conversion efficiency of greater than 2%

5. What are some of the other applications of nanocrystal solids?

As shown in chapter 5, a novel fabrication route was discovered to build heterojunctions from nanocrystal solids. The nanocrystal solids deposited as thin films were immobilized by chemical treatments to make them robust and insoluble. This allowed for multiple deposition of nanocrystal solids. Since each deposition is independent, the nanocrystals can be varied within the stack and as such an all nanocrystal heterojunction can be fabricated.

6. How to build an electroluminescent device from nanocrystal heterostructures?

An electroluminescent device works on the principle of recombination of electrons and holes. Once the procedure for fabricating heterostructures was discovered, it was only a matter of using different bandgap nanocrystals to achieve confinement of electrons and holes in the active layer. The nanocrystals with photoluminescence in the telecommunications wavelength of 1.58 $\mu$m were selected to construct the active layer. The electroluminescence device fabricated with all nanocrystal heterostructure was presented in chapter 5, with the efficiency of 0.5% and the emission peak at 1.58 $\mu$m.

While this project acted as proof-of-concept, the work has stimulated further research within the group. Efforts are already underway to standardize the field-effect measurements as a benchmark tool for performance of nanocrystals. The next section discusses future directions for this research and opportunities for improvement.

6.3 Future Directions and Closing Remarks

This project has opened many avenues of research towards the utilization of nanocrystal solids for fabrication of efficient devices. In the recent past, the group has had tremendous
success in fabricating solution processed optoelectronic devices from nanocrystal solids. While the devices were highly successful, a direct means to characterize the charge transport parameters was desired. The field-effect transistor devices have proven to be an excellent and reliable tool in characterizing the electrical performance of nanocrystals. This has created room for many fundamental studies to gain insight into device processing and synthesis procedure.

The electroluminescent device heterostructure still offer the possibility to be further optimized. Although it is a difficult challenge, the ultimate goal of the heterostructure architecture is to obtain electroluminescent lasing. In addition, it would be very interesting to observe n-type doping of nanocrystal solids to fabricate a p-n junction. In conclusion, this project demonstrates that there is a real opportunity to make bottom-up physical connection in order to achieve a top-down engineering goal.
Appendix A

Ligand Exchange Procedure

The following procedure is utilized to exchange the oleic-acid ligands on as-synthesized PbS nanocrystals with shorter butylamine ligands.

1. The nanocrystal solution is transferred into a test tube from the vial. The weight of the test tube is measured prior to the transfer.

2. The nanocrystals are then precipitated with methanol. A 4:1 volume ratio of methanol to nanocrystal is required.

3. The test tube is placed in the centrifuge for about 3 minutes.

4. The clear supernatant is removed as the nanocrystals precipitate to the bottom of the test tube.

5. The test tubes are then dried in the antechamber of the glovebox.

6. The weight of the test tube with dried nanocrystals is measured to obtain the total mass of nanocrystals.

7. The nanocrystals are then dispersed in a purified butylamine solution to a concentration of 100 mg/mL.
8. The test tube is stored in the glovebox for three days.

9. After three days, the nanocrystals are then dispersed into chloroform solution. First they are precipitated from butylamine solution with isopropanol. Then as described, above they are centrifuged followed by the removal of supernatant and drying in antechamber.

10. The final concentration is approximately kept to 100 mg/mL.

11. Often nanocrystals are filtered with 200 nm filters.
Appendix B

Photolithography Procedure

The following procedure is utilized to pattern field-effect transistor devices onto the silicon substrates after the deposition of gold. The lithography is done in the cleanroom.

1. The gold coated silicon substrate is cleaned sequentially with acetone, isopropanol, and deionized water.

2. The substrate is then dried on the hot place at 110°C.

3. The S1811 photoresist is spin-coated onto the substrate with following parameters;
   spin speed: 4000 RPM, acceleration: 12 s and spin time: 30 s.

4. The substrate is then dried on the hot plate at 110°C for 1 minute.

5. The mask aligner is used to pattern the substrate

6. The pattern is then immersed in the MF321 developer solution for 1 minute and rinsed with deionized water.

7. The substrate is then hard baked for 2 minutes at 110°C on hot plate.

8. Following the hard baking, the gold is etched with KI solution and rinsed with deionized water.
9. The final step involves the removing of resist with AZ300T resist stripper. The samples are immersed in the stripper solution for 10 minutes. This is then followed with rinsing in acetone and deionized water.
Bibliography


