Science and Applications of Infrared
Semiconductor Nanocrystals

by
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Abstract

In this work we study several applications of semiconductor nanocrystals (NCs) with infrared band gaps. In the first half, we explore the physics of two systems with applications in NC based photovoltaics. The physics of mixed films of CdTe and CdSe NCs is studied in chapter 2 as a model for NC based bulk heterojunction photovoltaics. We demonstrate that the presence of an active electron trap on the CdTe dramatically reduces the electron mobility in mixed films. The trapping state is linked to oxidation of the CdTe NCs. A cadmium oleate treatment is shown to reduce the oxidation rate. In chapter 3, we present a method to switch the carrier type of InAs NCs deposited in a thin film from p-type to n-type by the addition of cadmium. This provides a stable pre-deposition technique to control the NC carrier type and is a step towards pn homojunction based NC devices. We discuss the role that surface passivation and substitution doping may play in determining the carrier type. The second half explores the use of NCs for photodetector applications. Chapter 4 presents our efforts to move from a single pixel, proof of principle PbS NC infrared detector to a large area infrared imaging camera. A method to control the resistivity of the NC film through oxidation and re-treatment with ethanedithiol is presented. This allows for integration of our NC film with existing read out technology. The noise spectrum is shown to be dominated by 1/f noise and the dependence of the noise on the bias and channel length is determined. The detectivity is found to be determined by the carrier lifetime and dark current carrier density. In chapter 5, we demonstrate efficient UV-IR dual band detectors based on luminescent down conversion. In this design, NCs absorb UV light and re-emit the light in the infrared band of an InGaAs detector. The high quantum yields of infrared nanocrystals and unique absorption profile are shown to provide a significant advantage over organic dyes. The bandwidth of the detectors is measured and the effect of the down conversion layer on the spatial resolution is characterized.

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Chapter 1

Introduction

In this introduction, we will discuss the physics of three disordered systems: amorphous silicon, organic semiconductors, and semiconductor nanocrystals. Amorphous silicon is a well characterized disordered system, and many of the theories used for organic and nanocrystal systems were first developed for amorphous silicon. Organic semiconductors have emerged as a solution processable alternative to inorganic semiconductors for device applications including light emitting diodes, photovoltaics and transistors. A review of the transport physics of amorphous silicon and organic semiconductors is presented, followed by a current perspective on conduction in semiconductor nanocrystal thin films. In addition, several important concepts are presented in appendixes A through D. These include contact types (A), space charge limited currents (B), the statistical shift of the Fermi level (C), and the Franck Condon principle (D).

1.1 Amorphous Silicon

1.1.1 Introduction

The physics of crystalline semiconductors with long range lattice order and low defect density is the usual topic of introductory solid state courses. Concepts such as Bloch wave functions, k-space and the effective mass are all consequences of long range order
in the semiconductor. However, the fact that the material is a semiconductor is not a consequence of the long range symmetry in the device. In amorphous silicon (a-Si), where there is little order beyond the length scale of three Si-Si bonds a similar band gap is maintained as in a single crystal lattice. Understanding how disorder effects the properties of a-Si is the topic of this section. The theories developed for the well studied system of a-Si are often applied to organic and nanocrystal systems, both correctly and incorrectly. Understanding the origin of these models is important to understanding their applicability to other systems. The following discussion of amorphous silicon relies heavily on *Hydrogenerated Amorphous Silicon* by R. Street, which the author found to be a thorough but concise review of the physics and applications of amorphous silicon[1].

### 1.1.2 General Effects of Disorder

Although the term amorphous is applied to amorphous silicon, this does not mean that the atoms in the film take on random positions as though they were randomly packed spheres. The atoms in the material will form a local structure that attempts to satisfy the octet rule for each of the atoms. Si atoms will bond in a tetrahedral geometry. The difference from the crystalline lattice is that the bond angles are not at exactly 109.5 degrees, but vary around the ideal number. The local order of the Si is sufficient to generate a band gap in the material of a similar magnitude to the crystalline value. The lack of long range order makes the concept of a Bloch wave function invalid, which means that the concept of a momentum quantum number \( k \) is invalid. Instead of using the effective mass approximation, the density of states, \( N(E) \), must be described in more detail taking into account localized states that are created by the disorder as well as mid gap states created by dangling bonds. Since there is no longer a momentum quantum number, a-Si no longer has an indirect band gap. The lack of an indirect gap for a-Si does not necessarily mean a higher optical absorption coefficient. Optical transitions are discussed in terms of the density of states and the overlap between states, some of which are now localized states. The lack of overlap between localized states at large distances will result in a low matrix
element for these transition in the Fermi golden rule equation.

1.1.3 Deposition

The degree of disorder and the number of dangling bonds in the material are highly deposition dependent. Amorphous silicon (a-Si) and hydrogenated amorphous silicon (a-Si:H) can be deposited by a variety of techniques, with plasma deposition approaches being the most common. Using 'chemistry' terminology, these deposition methods deposit the film at a balance between kinetic and thermodynamic control. These terms are quite appropriate, as the formation of the film is a chemical reaction between the Si precursors and the Si on the surface. The corresponding terminology in a-Si:H deposition is physical vapour deposition (PVD) and chemical vapour deposition (CVD), which are kinetically and thermodynamically controlled respectively. Depending on the reaction conditions, different precursors will be created in the plasma which have significantly different reaction rates at the surface. If the reaction barrier is low, the precursor will immediately react upon reaching the surface, referred to as a high sticking coefficient. If the reaction barrier is higher, the precursor will find a more thermodynamically stable position to add to (low sticking coefficient), and a film with fewer dangling bonds will result. For a-Si:H, the main reactive precursor for the CVD process is believed to be SiH$_3$. The role of hydrogen in a-Si:H is complicated, but the main characteristics of hydrogen is its high diffusion constant in the films and ability to passivate dangling bonds. The single bond and small size of hydrogen allows it to form bonds with unpassivated Si atoms without greatly disturbing the surrounding local order. The result is a material with a much lower density of mid gap states. As discussed below, this allows for doping of a-Si:H which can not be done with a-Si due to Fermi level pinning in the mid gap states.

1.1.4 Doping

In the crystalline material, impurity atoms such as boron and phosphorus act as dopants when they replace a silicon atom in the lattice. In this position, the impurity
has 4 chemical bonds like the silicon atom it replaces and breaks the standard 'octet rule' of chemical bonding. The energy for the lattice to distort and rearrange to incorporate the impurity with the number of bonds to satisfy the octet rule is higher than the energy of the impurity atom with four bonds. In the case of the amorphous material, the presence of dangling bonds and structural disorder make it possible for the impurity to form more or less than the four bonds of silicon (i.e. 3 for boron, 5 for phosphorous). In this state, the impurity will no longer act as a dopant and will contribute density to the band structure rather than create mid gap states. This makes modulating the carrier density by the addition of dopant atoms challenging in amorphous materials. Even in a-Si:H that has been effectively doped, a majority of the dopant atoms do not take on the four fold bonding geometry of silicon but rather the 3 or 5 fold geometries that satisfy the octet rule and do not contribute to the doping. The presence of four fold coordinated dopant atoms may be due to a statistical probability of these higher energy states rather than this state being the energy minimum as is true in the crystalline material. As discussed in chapter 3, a nanocrystal system with a large surface area may exhibit similar chemistry. Unpassivated surface states and the ability to create surface reconstructions at lower re-arrangement energy than in the nanocrystal lattice may lead to preferential incorporation of impurities on the surface.

1.1.5 Band Structure

The band structure of a-Si differs from the bulk material in several important ways. For the bulk material, the density of states at the band edge is characterized by the effective mass of the closest conduction and valence band valleys. In amorphous materials, the density of states as a function of energy is more complicated and is generally depicted as shown in figure 1-1. Compared to the bulk material, the density of states is broadened near the optical band edge. More important from a perspective of conduction is the existence of the band tail states. These are a consequence of the disorder in the material, but these do not result from dangling bonds which are discussed below. The band tail consists of an exponentially decreasing number of
states with energies that deviate significantly from the band edge. The low density of these states means that they do not overlap with neighbouring states at the same energy and therefore do not form delocalized wave functions. Closer to the band edge the density of states increases until the states are no longer localized. The crossover energy from localized to delocalized is termed the "mobility edge". Above the mobility edge the states are delocalized and electrons have a greater mobility. Originally the mobility edge was thought to be an abrupt transition. Currently, it is considered to be a more gradual transition between localized and delocalized states. The simplification of an abrupt transition is sufficiently accurate for most calculations.

![Figure 1-1](image)

Figure 1-1: Cartoon of density of states for a-Si. The energy of the conduction and valence band are similar to the crystalline material. The band tail states lie at the edge of the conduction and valence bands. These are localized states. Dangling bonds lead to mid gap states which degrade performance. Hydrogen is used to reduce the number of dangling bonds (red line) by passivation in a-Si:H.

Dangling bond defects generate mid gap states as shown in figure 1-1. As discussed above, the synthesis of a-Si:H is tuned to reduce the density of these states, as depicted by the red distribution. Dangling bond states can be created by a photo-induced reaction after the material is made. This degrades the transport properties and limits the lifetime of the device. This increases the cost of a-Si based devices such as X-ray
imagers which require frequent replacement, and is one of the main problems with a-Si:H solar cells which must have long lifetimes (25 years) under high light levels.

1.1.6 Temperature Dependence of the Dark Current

Many of the models used to describe the temperature dependence of nanocrystal thin films are taken from the theory of amorphous materials. In particular, the dark current activation curves of NC films have been attributed to variable range hopping and Efros-Shklovskii variable range hopping. A general description of the conductivity is given by equation 1.1 where \( f(E, T) \) is the Fermi function and \( \mu(E) \) is the mobility of an electron with energy \( E \).

\[
\sigma = e \int N(E)\mu(E)f(E, T)\, dE
\] (1.1)

This equation gives the contribution from carriers at all energies to the total conductivity. At different temperatures and for different positions of the Fermi level, the conduction will be dominated by a particular portion of the density of states. At low temperatures if the Fermi level is far from the mobility edge in either the band tail or mid gap states then hopping conduction between localized states will dominate transport. There will still be a thermal activation component however, as excited carriers exist in a higher density of states. Transport is described by equation 1.2, where \( E_{tr} \) is a characteristic transport energy for conduction and \( \sigma_{otr} \) is the characteristic conductivity.

\[
\sigma_{tr} = \sigma_{otr} \exp[-(E_{tr} - E_F)/kT]
\] (1.2)

Since the mobility above the mobility edge is much greater than in the localized states, if a sufficient fraction of the carriers are thermally excited above the mobility edge then these carriers will dominate the transport, and the conduction can be described by equation 1.3, where \( \sigma_{oe} \gg \sigma_{otr} \).

\[
\sigma_{ext} = \sigma_{oe} \exp[-(E_c - E_F)/kT]
\] (1.3)
In a-Si:H and many other materials, the Arrhenius activation curves resulting from equation 1.2 and 1.3 follow the 'Meyer-Neldel Rule' which is discussed in detail in appendix C.

**Variable Range Hopping**

If the Fermi level is in the mid gap states or band tail of an amorphous material, at low temperature there will be negligible activation to the mobility edge and transport will be dominated by tunnelling between localized states. Near any given localized state \( S_i \), there will exist a distribution of other localized states \( S_j \) at distances \( R_j \) and energies \( E_j \) (figure 1-2). The tunnelling rate \( \nu \) between the initial state and another localized state is given by equation 1.4.

\[
\nu = C \exp(-2\alpha R_{ij}) \exp(-E_{ij}/kT)
\]

(1.4)

In equation 1.4, \( C \) is a constant and \( \alpha \) is the characteristic extent to which the wave function of the electron in a localized state falls off. Equivalently, \( \alpha \) can be expressed with the standard quantum tunnelling equation as shown in equation 1.5 where \( H \) is the tunnelling barrier height between states and \( m \) is the effective mass of the carrier.

\[
\alpha = \sqrt{\frac{2mH}{\hbar}}
\]

(1.5)

There are two exponential parts of the tunnelling rate. The first relates to the distance between sites and is temperature independent. The second relates to the energy difference between sites and is temperature dependent. At low temperature, the barrier to tunnel a greater distance to a lower energy state will be lower than the barrier to tunnel a shorter distance to a higher energy state. The result is that the average distance the electron tunnels is greater at low temperature as the electron 'seeks' a state that is closer in energy. As temperature increases, the energetic barrier is reduced and shorter tunnelling distances will be favoured. The relative probabilities of tunnelling to states of different energies and distance from the electron at low temperature and high temperature is depicted in figure 1-2.
Figure 1-2: (a) Cartoon of energy levels involved in variable range hopping. The density of states increases with the tunnelling distance. (b) Qualitative transition probabilities for low (blue) and high (red) temperature. The increased probability to hop a short distance at higher temperatures results in a decrease in the average hopping distance.

The average hopping distance and the temperature dependence of the conductivity where derived by N. F. Mott.[2] The variance in $E_i$ is characterized by the energy dispersion $W$. Let $R$ be the average distance between states and consider an electron at low temperature. The minimum barrier height will decrease as the number of states it can hop into increases, since there is a better chance of finding a state similar in energy. The number of states within a distance $pR$, where $p$ is a number, of the electron scales according to the volume of a sphere with the radius $pR$. The energy barrier in equation 1.4 can be expressed as $W/p^3$, since $p^3$ is a measure of the number of states that the electron can tunnel into within a distant $pR$. Substituting this into equation 1.4 gives equation 1.6.

$$\nu = C \exp(-2\alpha pR) \exp(-W/p^3 kT)$$

The most probable tunnelling distance can be found by maximizing equation 1.6, as expressed in equation 1.7.
\[
\frac{d}{dp}(2\alpha p R - W/p^3 kT) = 0 \tag{1.7}
\]
Solving equation 1.7 gives \( p^4 = 3W_D/\alpha kT \), with the most probable tunnelling distance being \( pR \). Inserting this into equation 1.6 gives the \( \exp\left(\frac{(-T_O/T)^{1/4}}{4}\right) \) temperature dependence that is characteristic of variable range hopping (VRH) as expressed in equation 1.8.

\[
\nu = C_1 \exp\left( -C_\alpha R \frac{3}{4} (W/kT)^{1/4} \right) \tag{1.8}
\]
VRH is well established for very low temperature conduction in a-Si and other disordered materials. Its application to NC systems at much higher temperatures is currently in debate[3, 4]. One issue is that the delocalization length in the NC system has often been taken as the nanoparticle size, since that is the approximate size of the carrier wave function. However, the delocalization length refers to the extent to which the wave function penetrates the barrier between states, which is much shorter[3].

The theory of Efros-Shklovskii variable range hopping was developed to explain the situation where the temperature dependence was found to vary as \( \exp[-(T_o/T)^{1/2}] \).[5] The essential result of Efros-Shklovskii VRH is that due to Coulomb effects, at very low temperature there exists a small gap in the density of states above the Fermi level of width \( \Delta \). Since there are no states to tunnel into within \( \Delta \) of the Fermi Level, the conductivity is reduced and the temperature dependence goes as \( \exp[-(T_o/T)^{1/2}] \), in between the \( \exp[(T_o/T)^{-1/4}] \) temperature dependence of VRH and the \( \exp[(T_o/T)] \) temperature dependence of Arrhenius activation.

**Photocurrent**

The absorption spectra of a-Si is similar to the bulk material, with increasing absorption at wavelengths higher than the band edge as the density of states increases. Excitons generated above the band gap will undergo rapid thermal relaxation compared to the time scale of either radiative or non radiative recombination. The possible
decay pathways for the exciton are illustrated in figure 1-3. The carriers will relax into the localized band tail states if the quasi Fermi level is below the mobility edge. If the mid gap defect density is low, then there is no path from the band tail states to the defect states due to separation in space. Capture by a defect state, which leads to non radiative recombination, is dependent on repeated thermal excitation of the carrier to the mobility edge from where it has a chance to be captured by the defect states (green arrows, figure 1-3(a)). As the temperature is reduced below 100 K, the thermal excitation rate is reduced and radiative recombination dominates as the main decay pathway. Carriers trapped in the band tail can recombined without thermal excitation to the band edge via a tunneling coupled radiative recombination process between the localized states. This rate of this process depends on the distance between the localized electron and hole and therefore the lifetime of the process can vary greatly from 10^{-8}s to 10^{-2}s.

Geminate recombination refers to the recombination of an electron and hole that were generated as part of the same exciton. Non-geminate recombination occurs when the electron or hole recombine with a carrier generated by a different photon. Geminate recombination occurs if the electron and hole do not diffuse far away from each other during the thermalization process. Whether geminate or non-geminate recombination occurs will depend on the distance between the electron and the hole after the exciton relaxes. The binding energy of the exciton, the excess energy above the band gap that is dissipated, and the thermalization rate will determine the distance between the electron and hole after relaxation. If the binding energy is high enough to prevent exciton dissociation during the relaxation process process, the electron and hole will thermalize into nearby localized states in the band tail (black arrows, figure 1-3(b)). From these states tunnelling assisted geminate recombination will occur. If the binding energy is low or the relaxation process fast, the carriers will diffuse a greater distance from each other during relaxation (red arrows, figure 1-3(b)). The radiative lifetime will be longer and if the excitation level is sufficient, non-geminate recombination will occur. The result will be a switch from monomolecular recombination to bimolecular recombination.
1.2 Conduction in Polymers and Small Molecules

1.2.1 Structure

The structure of poly(3-hexylthiophene) (P3HT), a conjugated polymer commonly used for organic field effect transistors (OFETs) and organic photovoltaic applications is shown in figure 1-4(a). Neglecting the effects of disorder and vibrational relaxation (see the section below on polarons and polaritons) the wave functions of the exciton and charge carriers will be spread across the entire polymer and de-localized transport will occur. For the wave function to spread out between thiophene units in P3HT, the rings need to be co-planar, i.e. be arranged such that they are in the same plane. The terminology used in polymer systems to describe the number of successive co-planar units is the conjugation length. When the polymer is deposited on a substrate to form a thin film, a large amount of disorder will be introduced that will break the
long range order. The backbone will bend to minimize the Van der Waals potential in the system, and the conjugation length will have a distribution about an average length. In a purely amorphous polymer all of the states will be localized. This is a very important difference from amorphous silicon, where a mobility edge exists above which conduction is de-localized. The density of states for the amorphous polymer in the conduction and valence bands is approximated as a Gaussian curve.

![Figure 1-4](a) Structure of P3HT. The conductive co planar backbone is highlighted in green. The alkyl chains impart solubility and encourage π stacking. (b) Cartoon of π stacking in P3HT. π stacking leads to microcrystalline domains and enhanced mobility.

For amorphous silicon, obtaining high mobility films requires passivation of dangling bonds to raise the Fermi level near the mobility edge. The transport properties are highly dependent on the deposition conditions. Unlike a-Si, the covalent bonding structure of the polymers is determined prior to deposition. However, polymer films deposited under different conditions can exhibit orders of magnitude differences in the mobility. For P3HT, high mobility films are realized by the creation of micro crystalline domains with significant π stacking. For high mobility P3HT films, π stacking leads to another axis of de-localization and increases the film mobility. Figure 1-
4(b) depicts two thiophene chains interacting such that the coplanar units overlap. This structure is stabilized by electronic and Van der Waals interactions between the chains. The structure of P3HT, with the side chains coming off the edges of the backbone, allows for efficient \( \pi \) stacking. It has been shown that for P3HT the charge carriers are de-localized across several \( \pi \) stacked units.

In the polymer film, \( \pi \) stacking may occur within the same polymer chain or between polymer chains as depicted in figure 1-5. At the boundary between microcrystalline domains, efficient transport between domains can be realized by a low stacking angle (figure 1-5, arrow a) as opposed to a perpendicular stacking angle (arrow b). Inter crystal penetration of the polymer chains may also increase mobility, as depicted in figure 1-5 (arrow c). In general, a structure that allows for efficient transport within crystal domains and efficient coupling between crystal domains via interpenetration or low angle stacking will yield a high mobility film. The structure of the organic films is generally controlled by deposition conditions such as solvent choice and deposition method, as well as post deposition annealing.

Figure 1-5: Cartoon of conduction pathways in a polycrystalline polymer film.
1.2.2 Small Molecule Semiconductors

High mobility small molecule semiconductors also exist. The term "small" is a relative term, but it is understood to differentiate a molecule with a few conjugated rings from the high molecular weight polymers. Common small molecule semiconductors include pentacene, tris(8-hydroxyquinolinato)aluminium (Alq3), and N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD). Small molecule semiconductors are often deposited by vacuum evaporation, which is the main method for the creation of organic light emitting devices (OLEDs). High mobility films may be deposited from solution if sufficient solubility is obtained. Solubility is often realized by the addition of side chains, which may have negative effects on the transport properties. It is possible to grow and measure macroscopic, single crystals of certain small molecule semiconductors. This allows for a direct measurement of the conduction along the different orientations, and a difference in mobility along the different crystal axis has been observed[6].

1.2.3 Charge Transport

There exist a variety of models, many of them fairly complex, for transport in organic systems. For simplicity, we just consider a few important concepts. As mentioned above, in an amorphous polymer there are no extended states. The common model is based on the a-Si model for transport in the localized band tail. In this model, the higher energy carriers will be in a higher density of states and will be more conductive, but no mobility edge exists above which there are delocalized states with dramatically higher mobility. The mobility can be highly dependent on the carrier density, which is particular important for OFETs. As the gate bias is increased to put more carriers into organic semiconductor, the Fermi level is moves closer to the band edge. Therefore the activation energy is lowered and the mobility increases. At low temperature, the variable range hopping model is frequently employed to explain the conduction.

In microcrystalline polymer systems, such as highly ordered P3HT, it has been
suggested that mobility in the crystalline domains is sufficiently higher than the mobility in the band tails that the mobility edge model may apply. If the order of the organic semiconductor is sufficiently high, the effects of polaron transport may become relevant. Polarons and polaritons are discussed below.

1.2.4 Polarons and Polaritons

Appendix D discusses the origin of the Stokes shift and the Franck-Condon principle. In summary, the excited state of the dye molecule will relax through nuclear re-arrangement to a lower energy than the absorption HOMO-LUMO gap. Vibrational relaxation occurs in the polymer or small molecule film as well. Relaxation can occur around the exciton or around a charge carrier. The result is that even in a perfectly ordered polymer chain, the carrier can realize a lower energy by localizing in a subunit of the chain that has a rearranged nuclear coordinate. When the carrier moves along the polymer chain, it has to first surmount an energy barrier to entering into the ground state vibration configuration in the next subunit. The result is that there is a thermal activation to transport even in a perfectly coplanar polymer. The charge carrier, moving with its vibrationally relaxed nuclear coordinates is known as a polaron. The equivalent situation with an exciton is termed a polariton. The barrier to the movement of the polaron or polariton is described by Marcus theory which takes into account the reorganization energy necessary for the reactant state to have the same nuclear configuration of the product state.

1.2.5 Carrier Type

Doping in organic semiconductor systems remains a challenge. One doping method is the incorporation of small ionic molecules into the polymer. The disadvantage of this technique is that the molecules will have a non negligible diffusion rate, even at room temperature. A counter ion generated p-n junction can become homogeneous over time.

Historically, a large number of polymers have been observed to conduct holes in
an OFET but not electrons. It was presumed that these materials were inherently p-type. However, it has been demonstrated that many polymers previously suspected of p-type only behavior will conduct electrons in a FET geometry when low work function contacts are used for the source and drain and a dielectric which does not trap charges is used instead of SiOx[7]. SiOx is known to have electron traps at the surface, and since the accumulation layer is directly next to the surface these can effectively reduce the electron conduction. This suggests that many of the previous measurements on polymers were not measuring an intrinsic property of the material.

1.2.6 Voltage Threshold and Stress

Since one of the main areas of application for organic semiconductors is for thin film transistors (TFTs), a significant portion of the literature concerns FET operation. One issue is that during repeated operation, the threshold voltage for a thin film transistor (TFT) can begin to shift, known as bias stress. This occurs for both organic TFTs and a-Si TFTs. This is a significant problem for transistor applications, which require reproducibility. Many reasons for bias stress exist, with the general idea being that a certain amount of trapped charge builds up in the film or at the interface. Under pre stress conditions, a negative gate bias induces free holes in the film and the current is increased. If holes become trapped, when the gate is negatively biased a second time no additional holes will be drawn into the film until the positive charge left in the film is compensated by the gate. Another source of threshold shift are impurities in the organic or introduced by the gate dielectric. Mobile ions can diffuse through the film and compensate for the gate capacitance. Upon removal of the gate voltage, these impurities will take time to diffuse away from the dielectric. The bias stress can be reduce with time, by photoexcitation, or by applying a high enough positive gate bias. Over time, trapped holes may be thermally excited back to the valence band and collected. Illuminating the device or applying a positive gate bias will add electrons to the conduction band that can recombine with the trapped charges.
1.3 Semiconductor Nanocrystals

1.3.1 Introduction

Compared to the previous sections on amorphous silicon and organic semiconductors, this section on semiconductor nanocrystals will be far less authoritative. The body of work on conductivity in NC films is not only far smaller than the previous areas, but arguably most of the work has been focused on making efficient devices, rather than looking at conduction from a physics perspective. Many important and fundamental questions about conduction in this system remain unanswered.

One issue with understanding conduction in NCs is that, unlike a-Si, there are so many different NC systems that are being investigated. Using a few basic synthetic principles, chemists are currently creating an ever increasing library of semiconductors in the nanocrystal/collodial quantum dot form. The literature on polycrystalline films of different inorganic semiconductors demonstrates that the nature of the defect states will vary greatly between semiconductors. From the work done so far with different core materials, it is apparent that the nature of surface states changes with each NC core material. Surface passivation will also vary with ligand treatment, just as the addition of hydrogen to a-Si significantly effects the conductivity. In this review, I will focus on the transport properties of a few well studied NC systems: CdSe, CdTe, PbS and PbSe.

1.3.2 Density of States

The absorption spectrum provides information about the density of states at the band edge. Mentzel et. al. estimate that the dispersion in the conduction and valence band can be described by a Gaussian distribution with a width of $\approx 50 \text{ meV}$ from the width of the first absorption feature for PbSe\cite{3}. For NCs, transmission electron microscopy also provides a measure of the disorder in the material. An empirical relationship between the size and band gap has been determined for many NC materials. The distribution of states in energy can be estimated by the distribution in particle sizes.
from transmission electron microscopy and the effect of the size on the band gap. For example, Cademartiri et. al. give the position in eV for the first absorption feature of PbS NCs a function of radius[8]. For PbS QDs with an average radius of 3 nm and a size variance of 5% of the radius, the full width half max of the distribution in energy is $\approx 60$ meV. The density of states per cm$^3$ in the film can be approximated from the NC density and the degeneracy of the HOMO and LUMO states. Considered a close packed nanocrystal film of PbS NCs with a 3 nm radius and an interparticle spacing of 1 nm. The NC density is $\approx 4 \times 10^{18}$ cm$^{-3}$ and the density of states is $\approx 5 \times 10^{20}$ per cm$^{-3}$eV$^{-1}$ assuming a distribution 50 meV distribution in the energy of the valence band.

One unanswered question is what the absorption of a single NC looks like and how much of the width of the first absorption feature is due to the absorption linewidth of a single NC. The emission spectrum of a single NC at room temperature is broad, and the width of an emission spectrum of an ensemble of NCs is significantly broadened due to the single emitter linewidth, not just due to the NC size distribution[9].

The high surface to volume ration of nanocrystals and abrupt termination of the crystal lattice mean that dangling bonds are likely to play an enormous role in the conduction properties. The position of the Fermi level as measured by the temperature dependence of the dark current (see below) has yielded significantly different values for different NC cores. These values appear to be consistent for a particular semiconductor lattice across treatments and are likely due to the specific distribution of states associated with each NC surface.

### 1.3.3 Mobility

The most pronounced factor in determining the mobility of a NC film is the effect of the interparticle separation on the tunnelling barrier. An important breakthrough in NC film conduction was the use of ligand treatments to replace the long chain capping ligand used in synthesis with a shorter ligand to decrease the interparticle separations.[10, 11] Jarosz et. al. provided evidence that the dominate effect of cap exchange is a decrease in the interparticle separation[11]. The increase in conductivity
with decreasing ligand length can be understood in terms of a simple tunnelling model using the WKB approximation (equation 1.9)[12].

\[
|T(E)|^2 = \exp \left[ 2 \int_0^d \sqrt{\frac{2m}{\hbar^2}} (\phi(x) - E) \, dx \right]
\] (1.9)

The barrier potential is assumed to be a square barrier that is lowered by the voltage applied such that \( \phi(x) = \phi_0 - \frac{eV}{a} x \). The distance between particles is \( d \).

Leatherdale et. al. provide a model that also accounts for the energy (\( \gamma \)) required to break apart the exciton and overcome the coulomb potential to separate the charges. The final tunnelling rate is given by equation 1.10

\[
I(V) = \exp\left(\frac{-4\sqrt{2}\hbar^2 d}{3m(eV - \gamma)} \left[ \left( \frac{m\phi_0}{\hbar^2} \right)^{3/2} - \left( \frac{m(eV - \gamma)}{\hbar^2} \right)^{3/2} \right] \right) \frac{1}{1 + \exp\left(-\frac{\gamma - eV}{a}\right)}
\] (1.10)

Drndic ct. al. simplify equation 1.10 for the case of a high barrier height to give the relation in equation 1.11

\[
I(V) \propto \exp\left(\frac{V}{V_0}\right)
\] (1.11)

Equation 1.11 has been used to model the mobility for NC films of CdSe[13], CdTe[14], PbS (see below), and InAs (Chapter 3). While the applicability of the model has been broad, the underlying equation predicts a much larger value of \( V_0 \) than is found experimentally, so the fit is perhaps as much empirical as it is based in theory. A quantitative analysis that predicts the field dependent mobility is still lacking.

1.3.4 Photocurrent

Exciton Ionization

In order to generate photocurrent, the exciton generated by the absorption of light must be separated into free carriers. Carrier relaxation in NCs occurs on the sub ps time scale, despite the large separation between the 1S and 1P states which were initially expected to reduce relaxation time by the phonon bottleneck effect. Therefore, it is assumed that separation must occur from the exciton ground state.
Consider the system depicted in figure 1-6(a). This is a model for the decay pathways of an exciton generated in a nanocrystal. The radiative rate is \( k_r(T) \). The non radiative decay through state \( S_{nr} \) is \( k_{nr}(T) \). The rate of either the electron or hole leaving the NC to the neighbouring NC is \( k_S(V) \). The non radiative decay rate increases with temperature, perhaps due to an activation energy for trapping of the free carriers. The separation rate will increase with voltage as the tunnelling barrier is lowered.

![Diagram of exciton decay pathways](image)

**Figure 1-6**: Cartoon of exciton decay pathways in a NC film. (a) Model for CdSe NCs. Efficient carrier extraction is realized when \( k_S > k_r + k_{nr} \). (b) Model for CdTe. The addition of a recombination center increases the lifetime of the hole and allows for efficient low field carrier extraction.

As suggested by Leatherdale et. al., we can model the extraction efficiency, \( S \), by equation 1.12[12].

\[
S = \frac{k_S(V)}{k_S(V) + k_r(T) + k_{nr}(T)}
\]  

(1.12)

In butylamine treated CdSe NC films saturation of the photocurrent, indicating efficient carrier extraction, is realized at low temperatures. At room temperatures, even at high voltages the non radiative rate dominates over the extraction rate (figure 1-7(a)). Figure 1-7(b) shows the room temperature photocurrent - voltage curve for a
film of CdSe/ZnCdS core/shell nanocrystals. The organic ligands have been removed by annealing. Passivation of surface states reduces the non radiative decay rate and efficient extraction of the exciton is realized at room temperature. In region I, the photocurrent increases exponentially with voltage while $S < 1$. In region II, the free carriers drift in the field but the lifetime is still shorter than the transit time. In region III, saturation of the photocurrent occurs when the transit time is reduced below the lifetime and both carriers are extracted.

Figure 1-7: (a) Comparison of the photocurrent at 77 K (closed circles, black line) and at room temperature (open squares, red line). The non radiative rate is too high at room temperature to observe saturation. (b) The three regimes of conduction in CdSe/ZnCdS films at room temperature. Saturation is observed due to a decrease in the non radiative rate with overcoating of the core.

Figure 1-6(b) presents a slightly more complex system. An additional state, $S_t$, has been added. This state has a high capture rate for electrons in the conduction band ($k_t > k_{nr} + k_r$). Once the electron is captured, the rate of recombination with a hole in the valence band is low, $k_h \ll k_{nr}$. The chance to generate free carriers if given by equation 1.13.

$$S = \frac{k_S(V)}{k_S(V) + k_r(T) + k_{nr}(T) + k_t} + \frac{k_t(V)}{k_S(V) + k_r(T) + k_{nr}(T) + k_t} + \frac{k_S(V)}{k_S(V) + k_h}$$

(1.13)

The effect of state $t$ is to compete with the radiative and non radiative decay...
pathways for capture of the electron. If $k_t \gg k_{nr}, k_r$, then equation 1.13 reduces to equation 1.14.

$$S = \frac{k_S(V)}{k_S(V) + k_h}$$  

(1.14)

The result is that the lifetime of the hole in the valence band is extended. This is the case of conduction in CdTe NCs which is discussed in more detail in chapter 2. Oxidation of CdTe core NCs results in a dramatic reduction in the quantum yield. The new state added by oxidation clearly has a strong capture rate for one of the carriers, satisfying the relation $k_t \gg k_{nr}, k_r$. If the rate $k_h$ was fast, the effect of oxidation on the NC film would be to reduce the photocurrent. Instead, the photocurrent increases upon oxidation, suggesting that the mechanism just presented is appropriate.

1.3.5 Photocurrent Temperature Dependence

Figure 1-8 shows the temperature dependence of the photocurrent for PbS NC cores with a first absorption feature at 1300 nm. The photocurrent increases monotonically with temperature. At all temperatures, the photocurrent voltage curves are nearly identical (figure 1-8(b)) In figure 1-8(c) the photocurrent voltage curves are fit to equation 1.15.

$$I_{ph} = \frac{V}{R_o} \exp\left(\frac{V}{V_o}\right)$$  

(1.15)

Equation 1.15 assumes that the voltage dependence of the mobility can be described by the tunnelling model from equation 1.11 and assumes an ohms law current-voltage relationship[14]. The temperature dependence of the conductance $G_o = 1/R_o$ is shown in figure 1-8(d). An Arrhenius temperature dependence is observed across the temperature range. In other NC systems, the slope of the current versus inverse temperature curve will decrease at lower temperatures. The temperature activation may be due to a similar model of thermal excitation to a characteristic hopping energy as described for the a-Si and polymer systems above.

Figure 1-9 shows the temperature dependence of the photocurrent for large PbS
NCs with a first absorption feature at 1725 nm. The photocurrent increases to a maximum, and then decreases at higher temperatures[15]. This same effect is seen in InAs:Cd NCs as discussed in chapter 3. This occurs when the trapped electron is thermally excited out of the recombination state into the conduction band. It can then recombine with a hole in the valence band. In photoconduction terminology, the electron capture state has gone from being a recombination state to being a trap state. By fitting the photo quenching decay, the position of the electron trap state can be determined. For the case of these large PbS NCs, the position of the recombination center is found to be 43 meV above the valence band. One reason that
smaller PbS nanocrystals do not exhibit photoquenching at room temperature may be because the conduction band is further from the electron trap state due to the effect of confinement on the conduction band position, reducing the hole lifetime.

![Graph showing photocurrent as a function of bias and temperature for large PbS NCs and activation energy vs electric field.](image)

Figure 1-9: (a) The photocurrent as a function of bias and temperature for large PbS NCs displays a photoquenching regime. (b) Fit to extract the position of the recombination center relative to the valence band.

### 1.3.6 Dark Current Temperature Dependence

The dark current in CdSe films with symmetric gold contacts is negligible even at room temperature, likely due to blocking contacts forming with the NC film (see appendix A). For PbS, PbSe and CdTe NC films, gold appears to make ohmic contacts with the films. The model developed by the Porter et al. for the dark current in CdTe is presented below[14]. This is the model used in chapters 2 and 3. Figure 1-10 depicts the situation considered in this model. The activation energy of the acceptor state is $E_a$. When an electric field is applied, the valence band of the neighbouring nanocrystal is lowered to $E_V$ by the applied field. $E_V$ is given by equation 1.16 where $\ell$ is the distance between the acceptor state and the neighbouring nanocrystal and $\varepsilon$ is the electric field.

$$E_V = E_a - \varepsilon \varepsilon \ell$$  \hspace{1cm} (1.16)

Figure 1-11(a) shows the temperature dependence of the dark current for PbS NC
films at different bias voltages. In figure 1-11(b) the scaled current voltage curves are shown for each temperature. Unlike the photocurrent curves for which the field dependence is constant, a clear temperature dependence of the current voltage curve is observed. This is attributed to a decrease in the activation energy of the carriers due to the applied bias as shown in figure 1-10 and expressed by equation 1.17.

\[ I_d = \frac{V}{R_o} \exp \left( \frac{V}{V_o} \right) \exp \left( \frac{e \varepsilon \ell - E_a}{kT} \right) \] (1.17)

The high temperature region is fit to the Arrhenius equation and the voltage dependent activation energy \( E_V \) extracted. A plot of \( E_V \) versus electric field is shown in figure 1-11(c). The intercept gives a value for the zero voltage activation energy \( E_a \) and the activation length \( \ell \) is extracted from the slope. In this case, \( E_a = 208 \text{ meV} \) and \( \ell = 6.5 \text{ nm} \). The activation length has been consistently found to be on the order of 1-7 nm for different NC systems.
Figure 1-11: (a) Temperature and bias dependence of the dark current in a PbS NC film. (b) Scaled IV curves demonstrate a change in the field dependence with temperature. (c) Extraction of the zero voltage activation energy and activation length with a plot of $E_V$ versus electric field.
Chapter 2

Conduction in mixed films of CdSe and CdTe Nanocrystals

2.1 Preface

Following the work on the photoconduction properties of CdSe NCs by Leatherdale[12] and Jarosz[11] and the transport properties of CdTe by Porter[14], considerable interest developed in type II structures of CdSe and CdTe. The heterojunction between CdSe and CdTe, as depicted in figure 2-1, is such that an exciton in either material can obtain a lower energy state by dissociating across the interface. For CdSe nanocrystals, both the temperature dependence and the IV curves indicated that breaking apart the exciton before it recombined in the NC at room temperature was a limiting process for efficient photoconduction. By creating mixed films of CdSe and CdTe NCs, it was believed that the voltage required to efficiently break apart the exciton would be lowered or even eliminated. Bulk heterojunction organic solar cells that make use of a type II band alignment, such as the ubiquitous P3HT:PCBM blend, have resulted in record organic efficiencies.

Kim et. al. developed CdTe/CdSe core shell NCs which showed type II emission[16]. This occurs when the electron resides predominately in the CdSe and the hole in the CdTe, and emission occurs with an energy corresponding to the LUMO of the CdSe and the HOMO of the CdTe. Halpert et. al. developed CdSe/CdTe nanobarbells con-
Figure 2-1: Type II band alignment of CdTe and CdSe NCs. Values are for the bulk semiconductor.

sisting of CdSe rods with a CdTe NC attached at each end[17]. With sufficient surface passivation, these also exhibited infrared emission. Without surface passivation, the quantum yield of these particles was very low, which will be relevant in the discussion below. We chose to do our work with films of mixed CdSe NCs and CdTe NCs and with CdSe/CdTe nanobarbells. At the time, we felt that the hole would be trapped in the CdTe core of the core/shell nanocrystals due to the increased tunnelling barrier presented by the CdSe shell between the CdTe cores. In retrospect, after the work on CdSe/CdZnS core/shell nanocrystals in which efficient conduction was found after complete ligand removal, the CdSe/CdTe core/shell system would have been interesting as well. This is particularly true since the shell may help to passivate the CdTe surface states, which we will show limit the photovoltaic performance of these devices. I would like to dedicate this chapter to Venda Porter, who was a wonderful and patient mentor. This chapter includes her work, as well as contributions from Tamar Mentzel, Jon Halpert, Marc Kastner and Moungi Bawendi.

2.2 Introduction

There is considerable interest in colloidal semiconductor nanocrystals (NCs) as active components for the next generation of solar cells and other optoelectronic devices. Clear potential advantages of colloidal NCs are that they can be deposited on any surface and that the band gap of a NC can be tuned by changing the size of the particle.[18, 19] However, with the advantages of NCs come serious challenges
because the organic ligands, which allow for the solution processing of the NCs, inhibit exciton separation and decrease charge carrier mobility in close-packed NC films.[13, 11, 20, 12, 21, 22] The large surface to volume ratio of the NC also results in more unpassivated surface atoms, which may serve as trap states, than would be present in a bulk semiconductor film. Such traps increase the probability for recombination in the bulk of the film, rather than extraction at the electrodes.[23]

The band gap of CdTe NCs can be tuned from 1.5 to 2.1 eV,[19] covering most of the range of the peak emission power of the solar spectrum.[24] CdSe/CdTe heterojunction solar cells displaying 2.9% efficiency processed from sintered NCs have been reported;[25] however, this value is still low when compared to the 16.5% efficiency which has been reported for CdTe/CdS thin film solar cells[26] and 13.6% for thin film CdTe solar cells on flexible substrates.[27] In addition, this efficiency is not achieved until the NCs are sintered together, burning away most of the organic ligands in the process, losing the quantum mechanical confinement and effectively creating a nanocrystalline thin film.[25] While spinning NCs from solution and then sintering may constitute an alternative route to bulk semiconductor thin films, many of the potential advantages offered by quantum confined NCs are lost in the process. In order to increase the efficiency of NC photovoltaic and other optoelectronic devices, the physics of charge transport through NC films needs to be well characterized so that methods can be developed to improve the extraction of charge from NC films while keeping intact quantum confinement effects. In this paper, the photoconductivity of films composed of both CdSe and CdTe NCs, and CdSe/CdTe nanobarbells (NBs) is investigated. CdSe adjacent to CdTe forms a type II heterojunction, in which the band offset of the two semiconductors separates excitons at the interface, with electrons in CdSe and holes in CdTe. Infrared emission from type II core/shell CdTe/CdSe NCs demonstrates that the type II effect is indeed present in NC materials.[28] By mixing CdTe and CdSe NCs together, numerous type II interfaces are created throughout the film and charge transport can, in principle, proceed carried by electrons through a percolating CdSe network and holes through a CdTe network, reducing carrier recombination in the film. However, we find that
charge trapping at NC surface states overwhelms the effect of the type II interfaces. Specifically, an electron acceptor state on the surface of CdTe NCs is found to trap electrons in our thin film NC devices. We present a detailed characterization of the electrical consequences of this surface state in mixed CdTe/CdSe NC and CdTe/CdSe nanobarbell photoconductive and photovoltaic devices.

2.3 Device Structures

Two measurement devices were used in this study. 1) The lateral device [Figure 2-2(a)] was a silicon inverted field effect transistor (FET). The FETs were fabricated by lithographically patterning gold bar electrodes 200 x 800 x 0.1 μm³ on 330 nm thick silicon oxide. The electrodes were separated by 1 or 2 μm. 2) The layered device [Figure 2-2(b)] consisted of a transparent bottom electrode; 20 nm poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) spin-coated onto indium tin oxide (ITO). The photo active layer consisted of multiple, discrete, 25 nm thick layers of CdTe NCs, CdSe NCs or CdSe/CdTe NBs spun from chloroform and treated with a solution of butylamine in acetonitrile to decrease interparticle spacing. The top electrode was a eutectic gallium indium solder (EGaIn).[29]

The film treatment employed in this paper is post-deposition cap exchange with butylamine[11]. For the butylamine cap exchange, the NC film was soaked in a 0.1 M solution of butylamine in acetonitrile for 2 min. The film was then rinsed in acetonitrile and baked in a nitrogen environment for 1 hr at 70 C to remove excess solvent.
Figure 2-2: Schematic of the devices used in the experiments. (a) Lateral device structure consisting of gold electrodes 200 X 800 X 0.1 \( \mu m \) patterned on 330 nm silicon oxide on a silicon back gate or quartz (not shown). The electrodes are spaced by 1 or 2 \( \mu m \). The NC film, typically 100–200 nm thick, was drop cast or spun onto the device and covers the entire surface of the device. (b) Layered device structure used in the photovoltaic study. 20 nm thick PEDOT:PSS was deposited onto ITO covered glass. NC layers, each 25 nm thick, are spun on top of the PEDOT:PSS. The top contact was a eutectic gallium indium solder (EGaIn) which was set in a thin PDMS donut (3.5 mm O.D., 1.5 mm I.D.). The EGaIn settles in the area defined by the PDMS donut and forms a conformal contact with the NC film. The EGaIn was contacted with a Pt wire and the ITO with a metal pin. Photoexcitation occurs through the ITO face of the device.

2.4 Results

2.4.1 Conductivity of Mixed Films of CdTe and CdSe NCs and Films of CdSe/CdTe NBs

Figure 2-3 shows the field dependence of the photogenerated current for films composed of varying ratios of CdSe NCs to CdTe NCs in the lateral device geometry (Figure 2-2(a)). Films containing only CdSe NCs (trace a) show photocurrent saturation with electric field, indicating efficient extraction of both carriers and blocking contacts, as discussed below, while films containing over 20 % CdTe NCs by volume (traces d-i) exhibit photoconductive gain and do not saturate with electric field in the field range studied. Films with a small percentage of CdTe NCs (traces b and c) show decreased photocurrent compared to the pure CdSe NC film and no longer exhibit saturation under the fields used in this study. The magnitude of the photocurrent reaches a minimum at 20 % CdTe NCs by volume, as shown in the inset of Figure...
Figure 2-3: Photocurrent versus electric field with 32 mW/cm$^2$ 514 nm excitation for mixed films composed of CdTe and CdSe NCs. Each line represents the photocurrent measured in a film containing a different ratio by volume of CdTe to CdSe: a) 100% CdSe, b) 14% CdTe, c) 20% CdTe, d) 33% CdTe, e) 50% CdTe, f) 66% CdTe, g) 80% CdTe, h) 88% CdTe, i) 100% CdTe. The left inset displays the magnitude of the photocurrent at $7 \times 10^5$ V/cm as a function of volume% of CdTe. The red lines and circles designate films in which the field dependence of the photocurrent resembles that of an all-CdSe NC film while the black lines designate those films in which it resembles the field dependence of the photocurrent through the all CdTe NC film. The right inset shows the photocurrent curves a, b and c plotted on a linear scale versus electric field, demonstrating the saturation of the 100% CdSe NC film and the loss of saturation with the addition of CdTe NCs.

Figure 2-4(a) shows the field dependence of the photocurrent of a CdSe/CdTe NB film compared to a CdTe NC film. The field dependence of the photoconductivity for films of CdSe/CdTe NBs is nearly identical to that of films composed entirely of CdTe NCs. In Figure 2-4(b) we show differential conductance measurements of the NB films as a function of the gate voltage (see Figure 2-2(a)). The dark conductance increases with negative gate voltage indicating that holes are the majority carrier.

The activation energy of the dark current in the CdSe/CdTe NB film is measured in the same manner as the activation energy of the dark current in CdTe NC films.[14] The current-temperature curves are shown in figure 2-5 for different biases and each curve is fit with the Arrhenius equation. The activation energy at each voltage is
extracted and that value is plotted verses field (Figure 2-5, inset) to extract the zero field activation energy. For the CdSe/CdTe NBs this value is found to be 0.33 eV, nearly identical to that of CdTe NC films[14].

2.4.2 Oxidation and Modification of CdTe NC surface

Figure 2-6 shows the dark conductivity and photoconductivity of a CdTe NC film as a function of field and air exposure. An increase in both the dark current and photocurrent is observed with increasing exposure time to air under ambient conditions, while the insets in Figure 2-6(a) and Figure 2-6(b) show that the overall shape of the field dependence remains largely unchanged.

In Figure 2-7, X-ray Photoelectron Spectroscopy (XPS) data for CdTe nanocrystal films processed under inert conditions are compared to identically prepared films exposed to air for three weeks. The 3.5 eV shift of the Te 4d spectrum upon oxidation is consistent with observations in reference [30] where a ~ 3.7 eV shift is proposed to correspond to Te in the +4 oxidation state and TeO$_2$ and CdTeO$_3$ are proposed as
Exposure of CdTe NCs in solution or in a thin film to oxygen results in rapid quenching of the photoluminescence. It has been shown that CdTe NCs with a Cd rich surface have a higher photoluminescent quantum yield (QY) in air than those with a Te rich surface.[31] After three precipitations and redispersion in hexane, the QY of the CdTe NC solution is 0.1%. However, we find that after addition of cadmium oleate the QY increases to as much as 50% and remains fluorescent for weeks when stored in air. To a 1 mL solution of CdTe in hexane, 20 μL of a 0.4 M cadmium oleate solution is added. The solution appears brighter immediately upon cadmium oleate addition and the fluorescence increases over time (Table 2.1). Figure 2-8 shows the dramatic change in the brightness of the CdTe NCs before and after Cd oleate addition. Fluorescence measurements were performed using a Horiba Jobin-Yvon Fluoromax-3 spectrometer. The fluorescence QY of CdTe NCs was calculated using oxazine 720 as the reference dye. The QY of this dye at room temperature is 60% in ethanol and 63% in methanol.[32]

While addition of the above cadmium oleate solution to the CdTe NC solution resulted in the greatest enhancement of CdTe NC fluorescence, other cadmium ligand
Figure 2-6: Room temperature dark (a) and photocurrent (b) current-field curves as a function of exposure to air. The electric field is swept from 0 to $10 \times 10^5 \text{ V/cm}$ for each curve. Two curves are taken at each air exposure time to demonstrate that it is the air exposure, and not sweeping of the electric field, which results in the enhancement of the current. The insets of graphs (a) and (b) are the same data scaled in current and plotted on a log plot to highlight the electric field dependence of the current. The current is measured in a cryostat under vacuum and then the sample is opened to air for the designated period of time.

<table>
<thead>
<tr>
<th>Cd source</th>
<th>Cores, crashed in N$_2$</th>
<th>2 mL TBP, 2 mmol DDA</th>
<th>2 mL TOP 2 mmol DDA</th>
<th>8 mmol oleic acid</th>
<th>8 mmol oleic acid 1 month</th>
</tr>
</thead>
<tbody>
<tr>
<td>QY (%)</td>
<td>0.1</td>
<td>31</td>
<td>29</td>
<td>23</td>
<td>50</td>
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</tbody>
</table>

Table 2.1: Quantum yield of CdTe NC solutions after the addition of a cadmium ligand complex. Cd 2,4-pentadionate is mixed with the listed chemical reagents at 100°C and then added to the core NCs under nitrogen.

complexes improved the fluorescence as well. However, only the CdTe NC solutions to which cadmium oleate has been added retain the fluorescent enhancement after precipitation. Tables 2.1 and 2.2 list the composition of the solution and the resulting QY of the CdTe NC solution.

When cadmium oleate is added to NCs that have been process in air, the fluorescence of the CdTe NCs quenches rapidly in air. When cadmium oleate is added to the oxidized CdTe NCs a small amount of QY is recovered, but the QY remains low (Table 2.2). A potential model for this system is that CdTe NCs precipitated in an inert atmosphere have many unpassivated Te atoms (some oxidized and some not) on the surface that serve as non-radiative pathways for exciton decay.
Figure 2-7: XPS spectra for a CdTe NC film before (grey line) and after (black line) exposure to air for three weeks. Characteristic Te 4d, Te 3d, and Cd 3d peaks are shown before (grey) and after (black) oxidation of the CdTe NC film. The unoxidized Te 4d doublet located at 40.73 and 42.2 eV is assigned to Te-Cd in accordance with bulk CdTe values.[30] In the Te 4d and Te 3d spectra of the oxidized film additional peaks appear shifted ~ 3.5 eV to higher binding energy. These are attributed to TeO$_2$ and CdTeO$_3$ surface states. The Cd 3d peak shows only a slight shift to higher energies, possibly due to Cd-O formation or oxidation of the ligands which are bonded to the Cd.

The cadmium ligands are added they passivate the Te atoms and the QY increases. However, if the Te atoms have been oxidized, the cadmium ligand cannot bind to the Te and the exciton non-radiatively decays through coupling to a Te-O state. XPS is used to characterize the surface of the Cd oleate passivated CdTe NCs. In Figure 2-9, characteristic XPS peaks (Te 4d, Te 3d, and Cd 3d) are shown for CdTe NC and CdTe NC with cadmium oleate films after oxidation. There is an Te-O peak present in Te 4d and Te 3d spectra for both NCs films indicating the presence of cadmium oleate does not prevent oxidation of Te. However, the ratio of the Te-O to Te-Cd

Figure 2-8: Image of a dilute solution of CdTe NCs in hexane with (black cap) and without (white cap) the addition of cadmium oleate. The two vials are photographed with (left) and without (right) UV excitation. These solutions are of the same concentration and have been stored in air for three weeks.
Table 2.2: The fluorescence quantum yield is shown for the addition of the stated reagent to a CdTe NC solution which has been processed in air.

Peaks is different for the two treatments as there appears to be a lower ratio of Te-O to Te-Cd in films treated with cadmium oleate.

Figure 2-9: XPS spectra of a CdTe NC film (black line) and CdTe + cadmium oleate NC film (grey line) after oxidation for three weeks. Spectra are provided for the Te 4d (top left), Te 3d (top right), and Cd 3d (bottom) states. Preparation of NCs for spin coating

2.4.3 Layered CdTe and CdSe Nanocrystal Thin Films Photovoltaics

Three layered device structures with CdTe and CdSe NCs and CdTe/CdSe NBs have been constructed. In each device the bottom contact is a transparent electrode, indium tin oxide (ITO) coated with 20 nm of PEDOT:PSS; each nanocrystal layer is 25 nm thick, and the top electrode is a gallium indium eutectic solder (EGaIn). The ITO is connected to ground and voltage is applied to the EGaIn contact. In contrast to the previous experiments, all measurements here are conducted in air. Device 1 consists of ITO, PEDOT:PSS, a CdTe NC layer (band edge absorption at 660 nm), a CdSe NC layer (band edge absorption at 600 nm), and EGaIn, in that order. The band diagram, depicted in Figure 2-10a), shows the positions of the work functions and conduction and valence bands for the metals and semiconductors respectively. These values represent the individual material properties prior to establishment of a uniform Fermi level across the device. The photocurrent action spectra (PCA) and
absorbance spectrum for this device are shown in Figure 2-11(b). Comparison with the absorption spectra of CdSe NCs and CdTe NCs (Figure 2-11(a)) shows that at zero bias the photocurrent comes primarily from the CdSe NC layer and there is little contribution from the CdTe NC layer. The limited contribution of CdTe NCs to the photocurrent is not a consequence of optical screening by the CdSe layer since the CdTe layer absorbs to the red of the CdSe layer, as indicated by their respective solution phase absorption spectra in Figure 2-11(a). When 0.6 V is applied to the EGaIn, the device is in reverse bias and the PCA spectrum still appears to only come from CdSe NCs. However, when -0.6 V forward bias is applied the majority of the photocurrent in the PCA spectrum comes from excitons absorbed in the CdTe layer.

Figure 2-10: Energy level diagrams for a) device 1, b) device 2 and c) device 3. Energies are given relative to vacuum level, and represent the values for each component prior to establishment of a uniform Fermi level across the device (band bending). For the ITO and EGaIn electrodes, the lines indicate the work functions of the metals. For the semiconductor materials, the bottom of the rectangle indicates the position of the valence band, and the top of the rectangle indicates the position of the conduction band. The dotted line indicates the position of the proposed electron trapping state on the CdTe NC surface. All devices exhibit diode behavior, and the arrows indicate the direction of forward bias in each device (see discussion).

Device 2 is a variation of device 1 with the order of the NC layers reversed; it consists of ITO, PEDOT:PSS, a CdSe NC layer, a CdTe NC layer, and EGaIn in that order (Figure 2-10(b)). At zero bias the photocurrent flows in the opposite direction of device 1 and the external quantum efficiency (EQE) is an order of magnitude lower, as shown in Figure 2-11(c). Like device 1, the PCA spectrum indicates that only excitons generated in the CdSe NC layer contribute to the photocurrent at zero bias while under forward bias, which corresponds to positive voltage applied to the EGaIn
Figure 2-11: (a) The absorption spectra of CdSe and CdTe NCs in solution. (b) The PCA spectra for device structure 1 is displayed at 0 V (black line), +0.6 V (black line, same as 0 V), and 0.6 V (grey line). The absorbance of device 1 is given by the dotted line. (c) The PCA spectra for device 2 is displayed at 0 V (black line) and +0.6 V (grey line). The absorbance of device 2 is given by the dotted line. (d) The PCA spectra for device 2 is displayed at 0 V (black line) and +0.6 V (grey line). The absorbance of device 2 is given by the dotted line.

for device 2, a contribution from the CdTe NC layer is clearly visible. CdSe/CdTe NBs are included in device 3 which consists of ITO, a CdTe NC layer, a CdSe/CdTe NB layer, a CdSe NC layer, and EGaIn in that order (Figure 2-10(c)). Like device 1, device 3 is forward biased when negative voltage is applied to the EGaIn. At zero bias the photocurrent comes mainly from the CdSe NC layer while under forward bias the NB and CdTe NC layers contribute to the photocurrent (Figure 2-11(d)).
2.5 Discussion

2.5.1 Conductivity in CdTe NC Films: A Review and further insights on Charge Transport Mechanisms in CdTe NC Films

Previous investigations of the dark and photo current in butylamine capped CdTe NC films between gold electrodes, differential conductance measurements have revealed that holes are the majority carrier of the dark current.[14] The room temperature dark current is found to be steady state, an indication that the gold electrodes can inject holes into the CdTe NC film, unlike the case of CdSe NC films[21]. This is consistent with the small (0.4 eV) difference between the work function of gold (5.1 eV) and the valence band of CdTe (5.5 eV). Holes are found to be generated by the thermal excitation of valence band electrons with a thermal activation energy of 0.38 eV, which we interpret as the energy difference between the acceptor state and the valence band (Figure 2-12). We now present an analysis of this state including its physical origin and its effect on the conduction mechanism of films incorporating CdTe NCs.

![Energy level diagram for a CdTe NC with an acceptor state 0.38 eV from the valence band denoted by $1S_h$. We ignore any intrinsic width of the valence and conduction bands. At room temperature this state can be populated with electrons (black circles) thermally excited from the valence band, leaving holes behind (white circles). As the temperature decreases, the number of electrons in the acceptor state (and thus the hole density) decreases.](image)

Figure 2-12: Energy level diagram for a CdTe NC with an acceptor state 0.38 eV from the valence band denoted by $1S_h$. We ignore any intrinsic width of the valence and conduction bands. At room temperature this state can be populated with electrons (black circles) thermally excited from the valence band, leaving holes behind (white circles). As the temperature decreases, the number of electrons in the acceptor state (and thus the hole density) decreases.
In bulk CdTe, a cadmium vacancy in the lattice results in an electron acceptor state located 0.3 eV from the valence band.[33] The surface of a CdTe NC contains tellurium atoms, many of which may be unpassivated. It is possible that unpassivated tellurium atoms, i.e. cadmium vacancies on the surface, or additional cadmium vacancies in the lattice are responsible for the electron accepting state in NCs. There is also evidence that an oxidized form of Te may be the acceptor state because the dark current increases with exposure to air as demonstrated in Figure 2-6(a). The XPS results (Figure 2-7) confirm that oxygen exposure alters the surface of the CdTe NCs, with clear new peaks in the Te 3d and Te 4d XPS spectra appearing after oxidation. These are assigned to Te in the 4+ oxidation state, consistent with TeO₂ or CdTeO₃ being the surface state.[30]

The CdTe NCs are kept under argon during synthesis, transferred to a nitrogen glove box for processing, and measured under vacuum in a cryostat loaded in the glovebox. However, none of these processes are fully oxygen free, and it is possible that some percentage of the surface tellurium atoms have been oxidized. In our proposed mechanism, prolonged air exposure creates more oxidized tellurium sites which can accept electrons from the valence band, and thus creates a larger density of holes. It should be noted that, as the inset of [Figure 2-6(a)] demonstrates, only the magnitude, and not the electric field dependence of the dark current varies significantly with oxygen exposure. In other words, oxidation of the CdTe NCs results in a higher hole carrier density but does not change the conduction mechanism.

The photocurrent in CdTe NC films is secondary with a photoconductive gain (number of times a charge carrier cycles through the device) greater than 1. This mechanism has been explored in detail in a previous publication.[14] In general, secondary photocurrents with gains greater than one occur when the electrodes can inject electrons and/or holes, and when the mobility of one of the charge carriers is higher than the other.[33] The carrier with the higher mobility cycles through the circuit until it recombines with the slower carrier or until the slower carrier reaches an electrode for extraction. Since the photocurrent is found to have a gain greater than one and, as discussed previously, only the hole is replenished from the gold elec-
trodes, the hole must have a higher mobility than the electron in CdTe NC films. This is surprising because in bulk CdTe the effective mass of the hole is 0.63 m₀, larger than the 0.11 m₀ effective mass of the electron.[34] This result can be explained if the electron accepting state at 0.38 eV accepts electrons from the conduction band as well as the valence band. When electrons are thermally excited from the valence band the state behaves as a doping state, increasing the hole density. However, when the state accepts electrons from the conduction band the electron is deeply trapped. This state is 1.4 eV from the conduction band so it is unlikely that electrons can be thermally excited out of the state, and therefore the average electron mobility is greatly reduced. Electrons remain in this state until they recombine with holes so the state could also be termed a recombination center with a minor affinity for holes.

This model is consistent with the effects of oxygen exposure on the dark and photogenerated current in CdTe films presented in Figure 2-6. A simultaneous increase in both the dark and photogenerated current may appear surprising, since an increase in the dark hole density should lead to a shorter lifetime of the electron in the conduction band, which in general results in a reduction in the photocurrent. However, if the acceptor state acts as a long lived recombination center for electrons, the addition of new acceptor states upon oxidation may actually extend the lifetime of the photogenerated electron, resulting in an increase in the gain and increased photocurrent.

In addition to altering the conductivity of CdTe NC films, air exposure strongly quenches the fluorescence of CdTe NCs, and this fluorescence quenching is correlated with the formation of oxidized tellurium atoms (Te-O) on the surface of the nanocrystal.[30] The fluorescence quenching may be a result of fast exciton dissociation due to rapid capture of the electron by the oxidized tellurium state. The post synthetic addition of cadmium oleate to CdTe NCs to form a cadmium rich surface is shown to increase the quantum yield of the CdTe NCs dramatically from 0.1% to 50% and reduce the rate of fluorescence quenching upon exposure to oxygen. If Cd atoms cover the surface, this could slow down the rate of formation of a Te-O complex on the nanocrystal surface, consistent with the increase in quantum yield and stability.
In summary, an electron accepting state on the surface of CdTe NCs is responsible for the p-type dark current because it accepts thermally excited electrons from the valence band, leaving holes behind. This same state may also be responsible for exciton separation by accepting electrons from the conduction band. These electrons remain trapped in this state until they recombine with a hole, offering an explanation for why the effective hole mobility is larger than the electron mobility in CdTe NC films.

2.5.2 Mixed Films of CdTe and CdSe NCs and CdSe/CdTe NB Films Between Lateral Electrodes  Photoconductive Mode

Films composed of mixed CdTe and CdSe NCs should theoretically aid exciton separation compared to pure films of CdTe or CdSe NCs because the two bulk materials form a type II junction when they are juxtaposed. Ideally, an exciton near the interface would be separated by the junction between CdTe and CdSe NCs, with the electron residing in the CdSe NCs and hole in the CdTe NCs after separation. The type II offset should reduce the voltage necessary for exciton separation and the resulting spatial separation of the charges should also increase the lifetime of the free carriers.

Saturation of the photocurrent with voltage, seen only in films of CdSe NCs (Figure 2-3), occurs when the transit time of the less mobile charge carrier is shorter than the recombination lifetime and the electrodes form blocking contacts[33]. If the mixed films of CdSe NCs and CdTe NCs were to exhibit saturation, it would indicate that the electrons were efficiently extracted from the mixed films. Because of the type II band offset, we would expect the CdTe NC / CdSe NC film to show photocurrent saturation at a lower applied field than for pure CdSe NC films, since the voltage required for exciton separation should be lowered by the type II interface and the recombination lifetime should be increased by the spatial separation between the electron and hole in the two types of NCs. The second requirement for satura-
tion, the presence of blocking contacts, is not satisfied for films of CdTe NCs. The observed photoconductive gain in CdTe NC films between gold electrodes indicates that gold does not form a hole blocking contact with CdTe NCs.[14] However, since the conduction band of CdTe NCs is 1.4 eV above the work function of gold, gold is expected to form a blocking contact for electron injection with CdTe NCs. In this case, once the electron lifetime is as great as the electron transit time saturation of the photocurrent should still be observed.

For the case of CdSe/CdTe NBs, the CdTe NC is directly connected to the CdSe nano-rods (NRs) which should increase the probability of type II exciton separation, since there is no longer an organic tunneling barrier between the CdSe and CdTe NCs, as is the case for the mixed films. In addition, the ratio of CdTe to CdSe is uniform throughout the film, eliminating potential difficulties stemming from segregation of CdTe and CdSe NCs.

The benefits of a type II heterojunction as discussed above are clearly not observed for films of mixed CdSe and CdTe NCs [Figure 2-3]. When the film is composed entirely of CdSe NCs, both the electron and hole can be extracted from the film; however, as the ratio of CdTe to CdSe NCs increases more electrons become trapped and the photocurrent does not saturate. When the film is about 33% CdTe NCs, the photocurrent vs. electric field curve closely resembles that of the 100% CdTe NC film indicating similar conduction mechanisms in both systems. From 33% CdTe NCs, increasing the percentage of CdTe NCs in the film increases the magnitude of the photocurrent as there are fewer CdSe NCs to slow the conduction of holes. CdSe NCs could in principle conduct holes, but the valence band is located 1.2 eV below that of CdTe and so extra energy must be supplied to conduct through the CdSe NCs. The minimum in conduction at 20% CdTe concentration is most likely a reflection of a percolation threshold in which CdTe NCs are spaced too far apart for hole conduction between CdTe NCs, but present in high enough concentration to lower electron mobility. Theoretical calculations of the percolation threshold for randomly packed hard spheres and closest packed hard spheres (NC films after chemical treatment or annealing likely exist somewhere between the two regimes) give a critical volume frac-
tion for percolation of 18% and 15% respectively, close to the minimum observed in the inset of Figure 2-3.[35] In CdSe/CdTe NBs films, where the CdTe concentration is well above the percolation threshold, a nearly identical field dependence of the photoconductivity to films of pure CdTe NCs is observed [Figure 2-4], indicating that for this material the CdTe trap state may be dominating the electron conduction.

Photo-excited electrons may enter the CdTe trap state directly from the CdSe conduction band since the energy of the CdTe electron trap state is lower than the energy of the conduction band of CdSe. Given the large energy offset between the CdTe and CdSe conduction band, it is unlikely that a free electron first hops into the CdTe conduction band before being trapped. However, exciton diffusion may also lead to decreased electron mobility in these films. In this model, the exciton diffuses from CdSe to CdTe NCs by Forster Resonance Energy Transfer (FRET). Efficient FRET transfer has been demonstrated in films of CdSe NCs[20] and films of CdTe NCs[36]. Since the band gap of CdTe is smaller than CdSe, there is no spectral overlap for the reverse process so the exciton becomes trapped in CdTe. The electron acceptor state may then directly trap the conduction band electron, breaking apart the exciton.

In conclusion, in both mixed films of CdTe and CdSe NCs and CdSe/CdTe NBs the electron trapping on the CdTe NC surface dominates charge transport through the films. Even if excitons are ionized at the type II interface, electron transport does not appear to be segregated to the CdSe NCs and NRs and electrons still end up deeply trapped at the surface of the CdTe nanoparticle.

2.5.3 Layered CdTe and CdSe Nanocrystal Thin Films Photovoltaics

While photoconductive devices with gains greater than unity can be useful for photodetectors, they do not increase the efficiency of a photovoltaic device. Unlike a photoconductive device, a photovoltaic device requires that both charges must be extracted at the electrodes. The low efficiencies of many NC/polymer hybrid solar
cells is attributed in part to trapping states in the NC/polymer film which cause charge carriers to recombine before they can be extracted at the electrodes.[23] The CdTe NC films and CdSe/CdTe NB films between lateral gold electrodes described above behave as secondary photoconductors with the hole amplifying the current as it cycles through the circuit a number of times before recombining with a trapped electron. If these materials are to work in a photovoltaic device, the electron must be able to reach an electrode for extraction.

The first device studied (Fig.2-10) is a type II planar heterojunction between CdSe NCs and CdTe NCs. The photoaction spectrum of the device reveals a minimal contribution to the photocurrent from the CdTe layer compared to the contribution from the CdSe layer. If excitons diffused efficiently to the interface from both layers and separated across the type II junction, then excitons created in both layers should contribute to the photoaction spectrum relative to the strength of their absorption. If the main source of free carriers is separation at the interface, then minimal contribution to the photocurrent from the CdTe layer suggests that the exciton diffusion length in the CdTe nanocrystals is much shorter than the diffusion length in CdSe. The dramatic quenching of photoluminescence of CdTe when exposed to oxygen indicates that the exciton lifetime is much shorter in air exposed CdTe NCs than air exposed CdSe NCs, which may result in a shorter diffusion length. The electrons trapped in the CdTe NCs are immobile and unable to reach the CdSe NC film to conduct, preventing photons absorbed in the CdTe layer from generating a current in the device.

Under forward bias, the contribution of CdTe NCs to the photoaction spectrum becomes apparent. In forward bias, holes can be injected from the ITO into the PEDOT:PSS and subsequently into the CdTe. This means that holes that recombine at the interface with electrons in CdSe can be replenished from the contacts, causing current to flow. Alternately, the current may arise from exciton separation at the interface with PEDOT:PSS, with the electron recombining in the p-type polymer. Either way, the effect of the photons absorbed by CdTe NCs is to increase the hole density in the CdTe NC film at equilibrium.
Device 2 is identical to device 1 with the exception that the order of the CdTe and CdSe NC layers are reversed. In this case, the built-in field created by the work function offset of the metal electrodes opposes the built-in field generated by the CdTe/CdSe heterojunction. The direction of photogenerated current flow at zero bias is reversed compared to device 1, indicating that the electrochemical potential difference between the CdSe NC layer and the CdTe NC layer is larger than that between the electrode materials. The EQE of device 2 is an order of magnitude smaller than that of device 1 as expected, given the non-ideal geometry of the device. As in device 1, the CdTe absorption only contributes strongly to the PA spectrum under forward bias, indicating that the behavior observed in device 1 is not unique to the CdTe NC and PEDOT:PSS interface.

Device 3 is identical to device 1 with the addition of a NB film between the CdTe and CdSe NC layers, forming a bulk heterojunction layer. Although the previous devices indicate that at zero bias the CdTe NC film does not contribute to the photocurrent, ideally the CdSe/CdTe NB film would exhibit better transport properties. However, as observed in the mixed NC films, the NB layer appears to act similarly to the CdTe layer since it does not contribute to the zero bias PA spectrum.

To summarize, the three photovoltaic devices with different combinations of CdTe NCs, CdSe NCs, and NBs all exhibit contributions to the photocurrent only from the CdSe NC layer when measured at zero applied bias. The CdTe NC and CdSe/CdTe NB layers contribute to the photocurrent only when the device is run in forward bias. These results are consistent with the trapping of electrons by the CdTe surface state described in the previous section.

2.6 Conclusions

We find that unpassivated and/or oxidized atoms on the surface of CdTe NCs serve to deeply trap electrons and enhance the exciton ionization rate. Experiments with mixed films of CdTe and CdSe NCs and CdSe/CdTe NBs in a planar device geometry all display conductivity properties that can be linked to the trapping of electrons on
the surface of the CdTe NCs. These trap states hinder CdTe NCs from contributing to the photocurrent in a NC based photovoltaic device at zero or reverse bias. These results demonstrate the importance of surface states in influencing the conduction in both homogenous and heterogenous NC based devices.

2.7 Experimental Information

2.7.1 Synthesis

CdTe and CdSe NCs were synthesized using standard methods for II-VI NC synthesis[14, 37]. The CdTe NCs were 6 nm in diameter and the CdSe NCs were 4.9 nm in diameter. In general, 1 mmol of cadmium 2, 4-pentanedionate (98%), 2 mmol of 1, 2-hexadecanediol, and tri-n-octylphosphine (TOP) is degassed for 1 hour at 100 C. This solution is cooled under argon, and 3 mmol of 1.5 M tri-n-octylphosphine selenide (TOPSe) or 1.5 M tri-n-butylphosphine telluride (TBPTe) is added. The chalcogenide donating precursor is the only difference between the syntheses of the two materials. The mixture is then loaded into a syringe and injected into a 360 C solvent solution consisting of 99% tri-n-octylphosphine oxide (TOPO), 90% hexadecylamine (HDA), and n-hexylphosphonic acid (HPA). The NCs are grown for 5-10 min at 260 C and then cooled to room temperature. Hexane is added to the room temperature growth solution and then it is transferred to the glovebox for storage.

CdSe/CdTe rod/dot nanobarbells (CdSe/CdTe NBs) were synthesized using a previously published procedure[17]. The nanobarbells consisted of CdSe nanorods (NRs) that were 15 nm in length and 5 nm in diameter with CdTe NCs at each end of each rod that were 5.5-6 nm in diameter. CdSe nanorods (NRs) are prepared by heating cadmium oxide (CdO), octadecylphosphonic acid (ODPA), and TOPO to 300 C in a 3-neck flask until the solution is clear. A solution of degassed toluene, TOP, and TOPSe is injected at 320 C, and NRs are grown at 260 C for 15 minutes. The rods are then precipitated twice from solution by adding methanol/butanol, centrifuging the solution at 3900 RPM, and redispersing in hexane. After the second precipitation, the
rods are dispersed in hexane, a few drops of octylamine are added, and the solution is allowed to sit for several days until there is a significant increase in quantum yield. Rods were then precipitated as above, dispersed in hexane, and filtered. To create CdSe/CdTe NBs, a mixture of TOPO, HDA and HPA is first degassed at 140°C and cooled to 80°C. Rods dispersed in hexane are added to the pot and the hexane is pulled off under vacuum. Meanwhile, a solution of cadmium 2,4-pentadionate, 1,2-hexadecanediol, and TOP is degassed at 110°C in a separate flask. After degassing, the solution is cooled and 1.5 M TBPTe is added to the cadmium solution. The resulting mixture is added dropwise to the pot at 260°C. The total reaction time after the start of the addition of the precursor solution did not exceed 15 minutes. The CdSe/CdTe NB solution is cooled and the NBs are then immediately precipitated by the addition of toluene to remove excess CdTe NCs from the NB solution. (The NBs are only soluble in chloroform.) CdSe/CdTe NBs appear to be light sensitive and fall out of solution if stored for several days in light. However, they are stable for months when stored in chloroform, in the dark, and in an inert atmosphere.

2.7.2 Cadmium Oleate Treatment

To prepare the cadmium oleate solution, 1 mmol of cadmium 2,4-pentadionate in 8 mmol of oleic acid is degassed at 100°C for about an hour. The temperature of the cadmium oleate solution is held above 60°C to prevent solidification before addition to the CdTe NC solution. The cadmium oleate solution can be stored as a solid in an inert atmosphere and warmed up for use in future experiments. All other Cdcontaining solutions are prepared by degassing 1 mmol cadmium 2,4-pentadionate with the listed chemical reagents at 100°C. Approximately 20 μL of each cadmium solution was added to 1 mL of CdTe NCs in hexane. The concentration of the CdTe NC solution is the same for all samples.
2.7.3 Film Preparation

CdTe and CdSe NC growth solutions are processed under nitrogen, in a glovebox, using previously reported methods to make close-packed films of NCs.[38, 11, 20, 12, 39, 22, 18] First, the sample is centrifuged and the supernatant saved. The precipitate consisting of TOPO and other salts is discarded. Next, the NC solutions are precipitated by adding methanol and spinning at 3900 rpm in the centrifuge. The supernatant is discarded and the NC precipitate is dispersed in hexane and butanol. This solution is then filtered through a 0.2 μm filter. The precipitation process is repeated two more times using 0.1 and 0.02 μm filters. For planar devices, after the third precipitation the NCs are dispersed in a mixture of 9:1 hexane:octane, rather than hexane and butanol. The solution is then drop cast onto the device. To make mixed films of CdSe and CdTe NCs the concentration of each solution is calculated using molar absorptivity values calculated empirically.[40] The appropriate amounts of each solution are mixed to give the desired ratio by volume of CdTe to CdSe in the film and solutions are drop cast on the devices. CdSe/CdTe NBs are not soluble in hexane, and so are dispersed in chloroform after each precipitation. As chloroform does not form smooth films via drop casting, NB films are spun onto both planar and sandwich device structures.

2.7.4 Planar Heterojunction Device Fabrication Details

PEDOT:PSS is a hole-conducting polymer which has been shown to smooth the surface of ITO. The NC layers, each 25 nm thick, were spin coated from chloroform and soaked in 0.1 M butylamine in acetonitrile for 10 minutes, and baked at 70 C for 1 hr in order to decrease interparticle spacing and make the films less susceptible to dissolving when the next layer is deposited. The EGaIn electrode wets the surface of the NC film and is contacted with a tungsten wire. The area of the EGaIn electrode is defined by a donut shaped stamp composed of a flexible polymer, cured poly(dimethylsiloxane), PDMS. EGaIn has a high surface tension and does not create shorts through pinholes in the NC film, thus improving the yield of working devices.
when compared to those constructed through evaporation of a top metal contact. In
addition, the EGaIn contact can be lifted off the film and moved to different areas on
the same film, allowing for the measurement of multiple junctions.[29]

2.7.5 XPS (X-ray Photoelectron Spectroscopy)

A Kratos AXIS Ultra Imaging X-ray Photoelectron Spectrometer with Delay Line
Detector is employed for XPS measurements. The excitation energy for all spectra is
1487 eV and data is taken in 100 meV steps. CdTe NCs are deposited in the glovebox
on a clean piece of polished n-doped silicon. Samples are removed and quickly taken to
the XPS for the measurement to limit air exposure. The samples are measured again
after storage in air for 3 weeks to observe the effects of oxidation on the composition
of the film.

2.7.6 Electrical measurements

The lateral FETs were attached to a 28-pin chip carrier and electrical contacts were
made from the electrodes to the chip carrier by gold wire bonds. Devices were tested
for leakage before film deposition by sequentially applying a high voltage (100 V) to
the source, drain, and gate electrodes. Devices with leakage greater than 0.5 pA were
discarded. The dark current at zero source-drain voltage $V_{ds}$ is very small. Therefore,
when measuring the gate voltage dependence an AC voltage is added to a DC $V_{ds}$.
This technique is the same as used to measure CdTe NC films in a previous study in
which a more detailed description of this measurement technique is provided[14].

All conductivity measurements on lateral devices were performed in a Janis VPF-
100 cryostat under vacuum. Samples were loaded into the cryostat in the glovebox
and never exposed to air. A Keithley 6517 electrometer was used to measure current,
$I,$ and apply voltage across the source and drain electrodes, $V_{ds}.$ An Agilent 6614C
DC power provides the gate voltage, $V_{g}.$ An Ar ion laser at 514 nm was used to
photoexcite the samples. It has been shown previously that photocurrent is not a
result of photoinjection from the electrodes.[12] For the layered devices, the current
was measured in air using the Keithley 6517 electrometer and voltage was supplied by a 7651 Yokogawa DC voltage source. The NCs were photoexcited with an Ar ion laser at 514 nm for I-V curve measurements. The sample was held perpendicular to the incident light with the light going through the ITO face first. The EGaIn electrode wets the NC film surface through a 1.5 mm radius hole cut in a thin piece of PDMS. Both the PDMS and EGaIn conformably contact the surface of the NCs. For photocurrent action (PCA) spectra measurements in which the photocurrent was measured as a function of the wavelength of the excitation light, the samples are photoexcited with a 150 W ozone free xenon arc lamp through a monochromometer. The photovoltaic and photoconductive external quantum efficiencies are determined using a silicon photodiode (Thor Labs DET210) as a reference. The absorbance spectrum of the NC films on glass slides was measured with a Cary 5000 UV-Visible-NIR Spectrometer.
Chapter 3

Conduction and Carrier Type in
InAs based Nanocrystals

3.1 Preface

In current NC literature, the lead chalcogenide nanocrystals are by far the most commonly used for applications in solar photovoltaics and infrared detectors. However, being the first widely used technology does not necessarily correlate to being the best technology in the long run. For example, \( \text{Cu}_2\text{S/CdS} \) solar cells were the dominate thin film solar technology for a period of time but have faded into obscurity and bulk \( \text{PbS} \) infrared detectors have fallen out of favour for infrared detection, For this reason, and out of scientific curiosity, we investigated InAs QDs.

One of the advantages to studying InAs QDs is the presence of significant literature on InAs nanowires. I was inspired to incorporate Cd into the nanocrystals based on the results of Hang et. al. [41] A considerable amount of literature exists for bulk InAs in the crystalline form as well, and a large amount of the literature focuses on the surface states that cause an accumulation on the bulk semiconductor surface. In this chapter, we present one of the first studies of the conduction properties of InAs NCs, and present what we believe is the first example of a method to switch the carrier type of a nanocrystal film in a stable manner prior to deposition. We feel this is the closest analogy to date to the standard methods of doping used in crystalline
and amorphous technologies. This work was done in close collaboration with Peter M. Allen, and I would like to acknowledge the help of all of those who contributed to this work: Liang-Yi Chang, Cliff R. Wong, Tim P. Osedach, Ni Zhao, Vladimir Bulovic, and Moungi G. Bawendi.

3.2 Introduction

Nanocrystal (NC) films have been proposed as an alternative to bulk semiconductors for electronic applications such as solar cells and photodetectors. One outstanding challenge in NC electronics is to robustly control the carrier type to create stable p-n homojunction based devices. We demonstrate that the post synthetic addition of Cd to InAs nanocrystals switches the resulting InAs:Cd NC films from n-type to p-type when operating in a field effect transistor. This method presents a stable, facile way to control the carrier type of InAs nanocrystals prior to deposition. We present two mechanisms to explain the observed switch in carrier type. In mechanism 1, Cd atoms are incorporated at In sites in the lattice and act as acceptor defects, forming a partially compensated p-type semiconductor. In mechanism 2, Cd atoms passivate donor type InAs surface states and create acceptor type surface states. This work represents a critical step towards the creation of p-n homojunction based NC electronics.

The ability to control the carrier type and concentration in bulk semiconductors with high spatial resolution is of fundamental importance for device fabrication. In contrast, the functioning of the majority of semiconductor nanocrystal (NC) based devices is dictated by the intrinsic carrier density as determined by NC surface states. For example, in the case of lead chalcogenide NC based Schottky junction solar cells the barrier height and depletion region are determined by the hole carrier density, which can be altered by changes to the surface chemistry such as oxidation.[42, 3, 43] The ability to control carrier type via the addition of stable donor or acceptor states to nanocrystals has been a longstanding challenge.[44]

The addition of charge carriers to nanocrystal films has been realized by sev-
eral distinct methods.[45, 46, 47, 10, 48] Direct charge addition has been accomplished through cyclic voltametry.[10, 48] Sodium biphenyl has been used to introduce electrons into CdSe NCs but the nanocrystal is quickly oxidized which removes the electron.[45, 49] Hydrazine post deposition treatments have been used to switch the conduction of PbSe NC films from p- to n- type, with the materials reverting to p-type conduction when the hydrazine desorbs from the surface.[46] Binary superlattices have been employed to remotely dope PbTe.[47] However, a stable, pre-deposition method to control the carrier type in NCs has yet to be reported.

In this work we demonstrate the ability to switch InAs NC films from n-type to p-type conduction through the incorporation of Cd. Cd is a stable transition metal cation that can be added to the InAs NCs prior to deposition. Films of InAs:Cd NCs demonstrate fundamentally different dark- and photo-conductive properties than InAs NC films, indicating that the incorporation of Cd has a large effect on the density of states within the bandgap. We also investigate InAs/CdZnSe core/shell NCs, where the III-V core is surrounded by a shell of II-VI atoms which pacify the surface and may act as donors and acceptors if incorporated into the III-V lattice. We find films of InAs/CdZnSe NCs exhibit ambipolar conduction when gated after annealing.

3.3 Results

3.3.1 Carrier Type

Bulk InAs has been shown to have an n-type surface accumulation region due to electron donating surface states.[50] For high surface area nanostructures, such as InAs nanowires, this results in inherent n- type conduction[51]. These surface states also lead to a large amount of Fermi level pinning at the metal contact, causing InAs to form ohmic contacts with many metals including gold[52]. Sulfur passivation or thiol treatment has been shown to reduce contact resistance and improve mobility in InAs nanowires.[51] For these reasons, ethanedithiol is chosen as the ligand for post deposition ligand exchange treatment.[53, 11, 54]
The gate dependence of nanocrystal films in a field effect transistor (FET) is commonly used to determine the film carrier type[3],[46, 14, 55]. The gate dependence and output curves of InAs core NC films are shown in figure 3-1a and 3-1b respectively. The InAs channel is n-type with clear hysteresis indicating trapping of the added charge. To reduce hysteresis, the gate voltage is pulsed to the measurement value and then back to zero between each data point.[14, 56] The NC film is on SiOx which is known to have electron acceptors at the surface and is therefore unlikely to give rise to the observed n-type behavior, suggesting this is a property of the NC film. The observed n-type conduction is in agreement with previous reports on the surfaces of bulk InAs[50] and InAs nanowires[51]. The positive threshold voltage is consistent with the filling of mid gap trapping states which may give rise to the observed hysteresis. At low and negative gate voltages, the output curves are supralinear. Supralinear conduction is commonly observed in nanocrystal films[3],[14] and is discussed below. At higher gate voltages, the source drain current increases sublinearly with voltage as the FET nears the saturation regime.

InAs:Cd NC films are prepared identically to the InAs core NC films as described in the experimental section. Figure 3-1c shows the effect of the gate voltage on the source drain current, and figure 3-1d shows output curves for the same device. A switch to p-type conduction is observed with considerable hysteresis even under pulsed gate conditions. For both InAs and InAs:Cd NC films the same gold contacts are used. The observation of n-type conduction in InAs NC films indicates that it is possible to inject electrons from the gold contacts into the NC film. P-type conduction in InAs:Cd NC films similarly indicates that hole injection from the electrodes is possible. Therefore the observed n-type and p-type behavior is attributed to the carrier type of the NC film, rather than presence of blocking contacts for either electrons or holes.

The switch of majority carrier from electrons to holes is due to acceptor states generated by the Cd incorporated into the NCs. We present two mechanisms to explain the observed behavior. In mechanism 1 (figure 3-2a), Cd occupies an In lattice position \((Cd_{In})\) as a substitutional impurity. Cd assumes the same bonding
Figure 3-1: (a) Dependence of source drain current on gate voltage for InAs NC films showing n-type behavior. (b) Output curves from the same InAs device. (c) Transfer curve for InAs:Cd NC films showing p-type behavior (d) Output curves from the same InAs:Cd device.

configuration as In in the lattice but due to its lower number of valence electrons creates an acceptor state impurity. Diffusion doping of bulk InAs has previously been accomplished using Cd$_3$As$_2$[57], which like Cd(oleate)$_2$ introduces the Cd into the lattice in a +2 oxidation state. The diffusion constant of Cd in bulk InAs at 300 C is $5.9 \times 10^{-14}$ cm$^2$/s.[58, 59] Therefore the diffusion length will be longer than the nanocrystal diameter even if the diffusion constant of Cd in the nanocrystal is three orders of magnitude lower than the bulk value. Substitutional incorporation of an impurity atom in a nanocrystal has previously been shown with EPR studies on Mn doped CdSe[60], and cadmium[41] and zinc[61] doping of InAs nanowires have been demonstrated. In mechanism 1, the switch from n- to p-type conduction does not require the added Cd to quench all of the donor sites (D1) on the InAs surface.
Instead, the Cd acceptor states (A1) over compensate the intrinsic donors, so that the number of acceptors is greater than the number of donors, NA ND. At thermal equilibrium, the donor electrons reside in negatively charged filled acceptor states (A1-) which act as hole traps, leaving behind positively charged empty donor states which can act as recombination centers for photoexcited electrons (D1+). In mechanism 2, (figure 3-2b) Cd atoms bound to the surface passivate the InAs donor state and create an acceptor state. For PbS and CdTe NCs, acceptor states have been associated with multi atom surface constructs such as PbSO₃ and PbSO₄ for PbS NCs[55] and TeO₂ and CTeO₃ for CdTe NCs[30]. As suggested for Cd doped InAs nanowires[41], the change from n-type to p-type may be a combination of mechanisms 1 and 2 where surface state passivation lowers the number of donor states and substitutional impurities create acceptor states.

Figure 3-2: Cartoon depiction of mechanisms for p-type doping of InAs:Cd nanocrystals. In mechanism 1, the addition of acceptors by Cd over compensates the electron donors on the surface, leading to a partially compensated semiconductor. In mechanism 2, the surface states are altered by the addition of a monolayer of Cd.

In this work we refer to the NC film carrier type, rather than the NC carrier type, to distinguish that we are measuring the property of a large number of nanocrystals that have undergone specific chemical treatments. The NC solution contains individual NCs that vary in composition and defect states and therefore it is misleading
to assign a carrier type to the NC solution. However, the properties of the NC film is governed by the overall distribution of defect states present, which can be altered prior to deposition, allowing for control over the film carrier type.

### 3.3.2 Characterization

InAs:Cd NCs were characterized by absorption spectroscopy, energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). EDS and ICP-AES are used to determine the amount of Cd present in the purified InAs:Cd NCs and give relative concentrations of In:As:Cd of 2.0:2.2:1.0 and 1.9:2.4:1 respectively (figure 3-3a). Based on the lattice constant of InAs and the 4 nm diameter of the NCs, we estimate that there are 600 In and 600 As atoms per NC, and that a monolayer of Cd atoms on the surface of the NC would add 320 Cd atoms. This gives a relative concentration of 1.9:1.9:1, in good agreement with the observed ratios if an As rich surface is assumed. The absorption spectra of InAs NC and InAs:Cd NC made from the same synthesis are shown in figure 3-3b and demonstrates that the InAs:Cd NCs maintain the original band gap and features of the InAs NCs with a slight broadening and a red shift of the 1S transition. If there was significant cation exchange due to the Kirkendall effect and formation of an InCdAs alloy it is unlikely the spectrum and band gap would remain consistent. The photoaction spectra of InAs and InAs:Cd NC films are shown in figures 3-3c and 3-3d respectively. The photoaction spectra demonstrate that the nanocrystals retain their confinement properties in the NC films after processing and ligand exchange. For InAs:Cd nanocrystals, an external quantum efficiency greater than 100 percent is observed, indicating gain greater than unity is occurring in these films.

It is apparent from the absorption and photoaction spectra that no bleaching in the first absorption feature is observed in solution or in the film for any of the NCs studied. A bleach in the first absorption feature occurs when a significant portion of the nanocrystals have one or more electrons in the lowest conduction band state or holes in the highest valence state. This results in a decrease in the probability of the optical transition between these two states, which is observable in the absorption
Relative Composition of InAs:Cd by Number of Atoms

<table>
<thead>
<tr>
<th>Type of Analysis</th>
<th>In</th>
<th>As</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS</td>
<td>2.0</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>ICPAES</td>
<td>1.9</td>
<td>2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Calculation for</td>
<td>1.9</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Monolayer of Cd</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-3: (a) EDS and ICP-AES composition analysis compared to the estimated composition for a monolayer of Cd absorbed to the surface (b) Absorption spectra of InAs and InAs:Cd showing retention of the InAs feature after synthesis of InAs:Cd. (c) and (d) are photoaction spectra for InAs and InAs:Cd devices on quartz demonstrating that confinement is retained in the NC films.

spectrum. For the case of InAs:Cd NCs, the lack of a bleach suggests the Fermi level lies too far away from the valence band for a significant percentage of nanocrystals to have a hole in the valence band at room temperature (or from a molecular perspective, to oxidize the HOMO level). This can be attributed to an acceptor state with an activation energy greater than kT or the presence of mid gap states which pin the Fermi level. This is similar to the case of lead chalcogenide NC films which have been well established to exhibit p-type behavior in a variety of devices without an observable bleach in the absorption or photo action spectra.

3.3.3 Activation Model of Dark Current Temperature Dependence

The comparison of the temperature dependence of the photocurrent and dark current between InAs and InAs:Cd NC thin films further demonstrates the effect of Cd incor-
poration on the conduction properties of the film. All temperature dependence data is taken on quartz substrates with films prepared identically to the corresponding field effect transistors. Figures 3-4a shows the dark current of an InAs NC film plotted versus temperature for several voltages. Various mechanisms have been proposed for charge transport in nanocystal films. We find our data to be best described by the model proposed for CdTe NC films.\cite{14} Similar to CdTe, InAs NC films exhibit a voltage assisted Arrhenius activation of the dark current. The increase in the dark current is caused by a simultaneous increase in the mobility and the carrier density. The photocurrent, which is proportional to the mobility, increases only by a factor of 2 over the same temperature region as the dark current increases by 3 orders of magnitude. Therefore the increased carrier density due to thermal activation dominates the dark current in this temperature range. Fitting to a simple Arrhenius activation model at different voltages, we find a strong voltage dependence on the effective activation energy. The voltage dependence derives, for the case of an n-type NC film, from the lowering of the conduction band of the neighboring nanocrystal relative to the energy of the electron donating gap state due to the electric field. This voltage assisted activation mechanism is modeled by equation 3.1, which gives a relationship between the effective activation energy, $\Delta E_a$, the activation distance, $a$, and the applied electric field, $E$.

$$J_{ph} = qFG = qF\frac{\mu V}{L^2}$$

(3.1)

Here $\rho_0$ is the intrinsic temperature independent resistivity of the film and $E_a$ is an empirically derived value that accounts for the nonlinear current-voltage characteristics of both the dark current and photocurrent. Fitting the InAs data to equation 3.1 gives an activation energy of 350 meV and an activation length of 2.4 nm (see experimental). The activation length is on the order of the interparticle spacing, consistent with the values obtained for CdTe. The activation energy reveals the energy of the closest electrons to the conduction band, and therefore gives a measure of the position of the Fermi level in the band gap. An activation energy of 350 meV is larger
than what might be expected for electron donors in InAs NCs, since for the surfaces of bulk samples the Fermi level is believed to be above the conduction band. The high activation energy can be attributed to the decrease in the electron affinity of the NC compared to the bulk due to quantum confinement, or the presence of mid gap states which pull the Fermi level closer to the middle of the band gap. Comparing the dark current activation for InAs and InAs:Cd, at higher temperatures the dark current in the InAs NC films continues to increase while the current saturates for the InAs:Cd samples. This saturation is attributed to complete ionization of the Cd acceptor states.

Figure 3-4: Temperature dependence of InAs dark current (a) and photo current (b) compared to InAs:Cd dark current (c) and photo current (d). NC films are measured on a quartz substrate with gold electrodes. InAs:Cd NC films show qualitatively different temperature characteristics from InAs, indicating a change in the population of mid gap states.
3.3.4 Modeling Photocurrent Temperature Dependence

Figures 3-4b and 3-4d show the temperature dependence of the photocurrent for InAs and InAs:Cd respectively. In general, the photocurrent density, $J_{ph}$, may be described by

$$J_{ph} = qFG = qF\frac{\tau\mu V}{L^2} \quad (3.2)$$

where $q$ is the electron charge, $F$ is the photoexcitation rate, $G$ is the device gain, $\tau$ is the lifetime of the majority carrier, $\mu$ is the mobility, $V$ is the applied voltage and $L$ is the channel length. For InAs NCs, the photocurrent is observed to increase with temperature. This can be attributed to an increase in the mobility of the carriers due to faster de-trapping times. As the temperature is increased, the de-trapping time is reduced, increasing the effective mobility by increasing the fraction of free carriers. For InAs:Cd, clear temperature dependent quenching of the photocurrent is observed at higher temperature. This photocurrent quenching is explained by the standard model for thermal quenching of a photosensitizing center.[62] In this model, the gain of a photoconductor decreases with increasing temperature as the minority carrier is thermally excited out of a recombination center. This can be understood in more detail by examining the temperature dependence of the carrier lifetime. If the contacts are ohmic the lifetime will be limited by the recombination time of the electron and hole and not by the transit time of the carriers to the electrodes. If the lifetime is longer than the transit time, then an internal quantum efficiency greater than unity may be observed. This is expressed as the gain of the device, which can be expressed as the ratio of the lifetime to the transit time of the device. For the case of InAs:Cd, high gain can occur if there is a state within the band gap that has a large capture cross section for electrons and, after electron capture, a small capture cross section for holes. This situation can occur for the case of a positively charged center which has a coulombic cross section for electrons. After electron capture, the state is neutralized and will have a neutral capture cross section for holes. This state, called a recombination center, effectively increases the lifetime of the carriers in the device.
and increases its responsivity.

Temperature dependent photocurrent quenching occurs when the recombination center is converted to a trap state. This occurs when the rate of the electron being thermally excited back to the conduction band, \( k_{\text{detrap}}(T) \), is greater than the chance of a recombination with a hole, \( k_{\text{rec}} \). This may be expressed, for the situation \( k_{\text{detrap}}(T) \gg k_{\text{rec}} \) as

\[
\tau = \frac{1}{k_{\text{rec}} + k_{\text{detrap}}(T)} \approx \frac{1}{k_{\text{detrap}}(T)} = \frac{1}{\nu \exp(E_r/kT)}
\]

(3.3)

where \( \nu \) is the attempt to escape frequency and \( E_r \) is the distance in energy of the recombination state from the conduction band. As the temperature increases, the effect of the recombination center decreases exponentially, resulting in an Arrhenius decay of the photocurrent as observed for the InAs:Cd samples. This is seen by combining equations 3.2 and 3.3. The high temperature InAs:Cd photocurrent data shown in figure 3-5 exhibits a good fit to this analysis. From the fit we determine an activation energy between 110-170 meV. We propose that the shallow sensitizing center identified here is the same center that acts as an intrinsic n-dopant in the InAs core NCs, state D1+ in figure 3-2a.

![Figure 3-5: High temperature photocurrent quenching data for InAs:Cd nanocrystals. The black lines are Arrhenius fits to the data.](image)

### 3.3.5 InAs/CdZnSe Core Shell NCs

The third InAs based NC system studied is annealed films of InAs/CdZnSe core/shell NCs. In order to improve photoluminescence properties, InAs particles are commonly
overcoated with a shell composed of CdZnSe.[63] As deposited core/shell NC films generally exhibit reduced conductivity compared to core NC films because of the increased core to core tunneling distance due to the shell and have attracted less attention than core NC films for electronic applications. However, thermally annealed CdSe/CdZnSe core/shell NC films with a 2-3 monolayer thick shell have been shown to maintain quantum confinement of the exciton and demonstrate improved photocurrent response over CdSe core NC films[64]. InAs/CdZnSe core/shell NCs are prepared from 4.1 nm cores and overcoated to reach a final size of 5.9 nm as determined by TEM. This is consistent with three monolayers of CdZnSe. Figure 3-6a shows the photoaction spectrum of an InAs/CdZnSe NC film after annealing at 300 C under vacuum of 24 Torr for 30 minutes, compared with the solution phase absorption spectrum. Confinement of the exciton is maintained, and the photocurrent response is similar in magnitude to the core NC films. The transfer curves for a 300 C annealed NC film (figure 3-6b) show ambipolar behavior, with the NC film being p-type at zero bias. The ambipolar behavior indicates that the density of mid gap states is low enough that the Fermi level can be raised from near the valence to near the conduction band by the applied gate voltage, which we attribute to surface passivation by the shell. The dark current temperature dependence shown in figure 3-6c fits well to the same model used for InAs NC, with an activation energy of 410 meV and activation length of 1.4 nm. The photocurrent temperature dependence (figure 3-6d) resembles that of InAs and does not exhibit a photocurrent quenching regime.

3.4 Conclusion

We have presented electrical characterization of thin films of InAs, InAs:Cd, and InAs/CdZnSe nanocrystals. In each case, the photoaction spectrum demonstrates that the NC films are photosensitive and retain the quantum confined properties of the NC. Consistent with the bulk and nanowire forms of InAs, InAs NC films exhibit n-type conduction attributed to electron donating surface states. The incorporation of
Figure 3-6: Electrical characteristics of InAs/CdZnSe core/shell NC films annealed at 300 C. (a) Photoaction spectrum compared to absorption in solution demonstrating confinement of the exciton after annealing. (b) Ambipolar NC film with p-type conduction at zero gate bias. (c) Dark current activation and (d) photocurrent activation curves shown on an Arrhenius plot at different source drain voltages.

Cd atoms prior to deposition results in p-type InAs:Cd films. This provides a facile, stable route for controlling carrier type of InAs NCs. We attribute the switch in carrier type to either generation of acceptor states when Cd substitutes for an In site in the NC lattice or creation of acceptor surface states by Cd. Ambipolar behavior is observed in annealed InAs/CdZnSe core/shell NCs. The results presented here motivate further investigation of transition metal impurity incorporation for carrier control in nanocrystal based electronics.

3.5 Experimental

3.5.1 Synthesis

InAs core and InAs/CdZnSe core/shell NCs were synthesized according to published procedures[63, 65, 66]. The chemicals used were tri-n-octylphosphine (97%, Strem),
tris(trimethylsilyl)arsine (Nanomems, France), Indium chloride (99.999%, alfa aesar), oleic acid (alfa aesar), octadecene (90%, Sigma), diethyl zinc (Strem), cadmium oxide (alfa aesar), and oleyl amine (Acros Organics). All manipulations were performed in a nitrogen filled glovebox or schlenk line using standard air-free procedures. For the InAs core synthesis, a stock solution of InCl$_3$ in tri-n-octylphosphine (TOP) was prepared by adding 3 grams of InCl$_3$ to 10 ml of TOP and heating to 270 C for one hour. To 1 ml of the InCl$_3$ stock solution was added 100 mg of tris(trimethylsilyl)arsine [(TMS)$_3$As], the resulting solution was injected into a rapidly stirring solution of 3.5 ml TOP at 300 C. The temperature was lowered to 270 C for growth of the InAs cores and subsequent injections. Secondary injections took place at 25 minutes, 50 minutes, and 75 minutes. Each secondary injection consisted of 100 mg of (TMS)$_3$As in 1 ml of TOP. For the InAs/CdZnSe synthesis, 2 ml of growth solution from the InAs core synthesis was purified by addition of anhydrous butanol and ethanol and subsequent centrifugation in an inert glove box. The InAs cores were redispersed in 2 ml of anhydrous hexanes. The solution of InAs cores was injected into a dry solution of 4 ml octadecene and 1.5 oleyl amine. This solution was degassed at 60 C for 30 minutes and then degassed at 100 C for one hour. Overcoating stock solutions consisted of 0.1 M diethyl zinc in octadecene, 0.2 M TOPSe in TOP, and 0.04 M cadmium oleate in octadecene. The reaction flask was then heated to 260 C for shell growth. Each injection was spaced by a 15 minute interval and were injected as follows: 2.5 ml of the cadmium oleate solution, 0.5 ml of TOPSe, 1.0 ml of diethyl zinc, 0.5 ml of TOPSe, 1.5 ml of diethyl zinc, and 0.75 ml of TOPSe.

To synthesize InAs:Cd NCs, a 0.2M solution of Cd(Oleate)$_2$ with oleyamine is prepared by adding 514 mg CdO, 2.5 ml oleic acid and 2.5 ml of oleyamine to 14.8 ml octadecene. This solution is put under vacuum for 1 hour at 100 C, heated under nitrogen to 280 C until the reddish CdO tint disappears, and then placed under vacuum for 1 additional hour at 100 C. Sufficient Cd(Oleate)$_2$ was added to the InAs growth solution to form approximately one monolayer of Cd on the surface of the InAs NCs, similar to the SILAR technique for overcoating.\[67, 68\] This solution is heated to 290 C for three hours.
Composition Analysis

Energy dispersive X-ray spectroscopy (EDS) was conducted with a JEOL 6320FV SEM equipped with an EDS detector. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is performed with an Activa system from Horiba Scientific. Samples were prepared by dissolving purified nanocrystals in a 3:1 mixture of hydrochloric acid and nitric acid (aqua regia) for 36 hours at 75°C. Aqua regia was prepared from TraceSelect Ultra grade chemicals from Sigma Aldrich to avoid sample contamination.

Film Processing

All NC film deposition and treatment was done in a nitrogen filled glovebox. Nanocrystals were purified from the growth solution according to published procedure with slight modification.15,17 The nanocrystals are precipitated three times by adding a mixture of ethanol and acetone to the nanocrystal solution and centrifuging. After each precipitation the NCs were redissolved in hexane and filtered through a 0.1 μm PTFE filter. The NC films were drop cast from a 10:1 hexane:octane mixture. Post deposition ligand exchange was done with 100:1 volume ratio of acetonitrile and ethanedithiol for 30 minutes, after which the NC films were rinsed with pure acetonitrile and baked at 100°C for 30 minutes. To fill in cracks created in the NC film during the first treatment, a second layer was drop cast and treated identically to the first layer.[46] For annealing studies, NC films were annealed under vacuum in a nitrogen glovebox. The NC films were held for 30 minutes at the specified temperature.

Substrates and Measurement

All data was taken using symmetric gold electrodes with a 5 nm chrome adhesion layer. Gold electrodes were deposited prior to nanocrystal deposition. For the photocurrent temperature dependence measurements, a quartz substrate was used. The electrode width was 800 μm, the height was 200 nm, and the channel length is as specified in the text. For gate effect measurements, the NC films were deposited on SiOx
on a p+-doped Si substrate. Unless otherwise noted, the electrodes were interdigitated fingers. Each interdigitated electrode had 60 channels of 1 mm channel width for a total channel width of 60 mm, a height of 50 nm, a channel length of 10 μm, and a 950 nm SiOx layer. The dark conduction data was measured with an Ithaco 1211 transimpedance amplifier connected to an Agilent 34401A multimeter. Photocurrent was measured using mechanically chopped (15 Hz) 514 nm laser excitation and a Stanford Research System 830 lock in amplifier. The NCs were kept under nitrogen or vacuum throughout the synthesis, processing, deposition and measurement steps.

**Arrhenius Activation Curve Fitting**

Figure 3-7a shows the temperature dependence of the dark current for InAs NC films as a function of the temperature and voltage. For clarity, only a subset of this data is shown in figure 3-4. The complete series of data points used to find the zero field activation energy is shown here with the corresponding Arrhenius fits. For each voltage, an activation energy is extracted from the Arrhenius fit and plotted versus electric field in figure 3-7b. We extract a zero field activation energy of 350 meV and an activation length of 2.4 nm. Figure 3-5c and 3-5d present the analogous results for InAs/CdZnSe.
Figure 3-7: Extraction of zero field activation energy for InAs and InAs/CdZnSe NC films. (a) Arrhenius fit for InAs for applied bias between 80 V and 200 V across a 2 micron gap. (b) Activation energy at different electric fields as determined by fits in (a). A linear fit gives the zero field activation energy and activation length. (c) and (d) follow the same fitting procedure as (a) and (b) for a 1 micron gap InAs/CdZnSe NC films.
Chapter 4

Quantum Dot SWIR Detectors

4.1 Introduction

4.1.1 Infrared Detector Background

Silicon based detectors dominate the market for imaging cameras in the visible region of the electromagnetic spectrum. One of the reasons that silicon technology is preferred for the detector pixels is that silicon is also used for the read out integrated circuit (ROIC) that converts the current in each pixel into an external signal. Since there is no lattice mismatch between the pixel element and the read out element, high quality silicon detector pixels can be grown directly on top of the ROIC. This reduces cost and increases production yield.

When the material for the pixel can not be grown in high quality on the read out circuitry, a common manufacturing technique is known as flip chip technology[69]. This is depicted in figure 4-1(a). The array of imaging pixels, known as the focal plane array (FPA) since it is positioned in the focal plane of the camera, is deposited onto the ROIC. In between the FPA and ROIC are indium bumps which form a malleable electrical contact. Precise alignment is required for this step. The drawback to this type of manufacturing is the cost of the FPA and the low production yield due to misalignment of the FPA and ROIC. Examples of FPA technology include InGaAs arrays for the short wavelength infrared (SWIR, 1-2μm) region and HgCdTe
for the mid wavelength infrared (MWIR, 3-5μm)[69].

Figure 4-1: (a) Cartoon of a flip chip InGaAs FPA detector interfaced to a Si ROIC with indium bumps. (b) Cartoon of QD SWIR detector design

In this chapter we explore QD based SWIR detectors. These show promise as a low cost, solution processable alternative to InGaAs FPAs. The emphasis is on developing methods to produce an actual QD based SWIR FPA, rather than on developing a 'proof of principle' single detector. Our design strategy is depicted in figure 4-1(b). QDs are deposited in a photoconductive geometry on a modified ROIC. This allows for complete fabrication of the readout and electrodes prior to QD deposition, after which the device is ready without further processing. The lateral geometry also prevents shorting from occurring.

Using a single pixel test structure, we present a method to controllably tune the resistance of the QD film to match the capacitance of the ROIC circuitry. The performance of the device is analysed as a function of voltage, channel length, operation frequency and excitation intensity. The noise spectrum is characterized and found to be dominated by 1/f noise. We characterize the voltage and channel length dependence of the 1/f noise and find that under low electric field, the detectivity is
independent of these parameters.

4.1.2 ROIC Capacitance

Figure 4-2(a) depicts the circuit diagram for the operation of a read out integrated circuit (ROIC) under non-constant bias. The initial charge on the capacitor $C$ is set to $Q_o$. As depicted in figure 4-2(b), the capacitor discharges through the photoconductor which has a resistance $R_d$ in the dark and $R_L$ under illumination. After an integration time $\tau$, the remaining charge $Q_\tau$ is read out. The fraction of charge remaining in the dark is given by equation 4.1 where $C$ is the capacitance of the ROIC.

$$\frac{Q_\tau}{Q_o} = \exp\left(-\frac{\tau}{R_d C}\right) \quad (4.1)$$

For a given capacitance, if the dark film resistance is too low, nearly all of the charge is depleted in the dark. When light is incident on a detector with low resistance, the change in the resistance of the photoconductor under illumination will not be detectable since the change in remaining capacitance is negligible. While $\tau$ can be varied, the minimum integration time is limited by the ROIC electronics, and maximum integration time is determined by the desired frame refresh rate. Therefore the capacitance of the ROIC circuitry sets a minimum resistance requirement for the detector pixel. QD detector pixels with high resistance can be made using QDs with long chain ligands such as trioctyl phosphine oxide (TOPO) and oleic acid[11, 12]. However, the increase in resistance is primarily due to a decrease in the mobility which will also decrease the EQE of the photoconductor. If the external quantum efficiency is too low then the decrease in resistance will be too low for detection under standard illumination conditions. System integration requires matching the resistivity and photo-sensitivity of the QD photo-conductive films with the read out circuitry. Regardless of the performance of the QD film in the lab, if $R_D$ is too low for the ROIC the dark current will saturate the circuitry. If the photosensitivity is too low, the signal will be too low to detect.
4.2 Results and Discussion

4.2.1 Controlled Oxidation to Tune the QD Film Resistance

In general, the current versus voltage curves for a QD film in the dark or under illumination will not be linear at high electric fields. However, for electric fields below 3 kV/cm, ohms law is obeyed for all of the PbS QD films studied in this chapter (see experimental). The dark current scales with the electric field for all channel lengths measured, and no significant contact resistance is observed. Therefore the current flowing through a detector pixel of any geometry is fully characterized by the film resistivity at low bias.

Figure 4-3 shows the effect of oxidation and subsequent ethanedithiol (EDT) treatment on the resistivity of our PbS QD photodetectors. The resistivity gives an intrinsic measure of the carrier density and mobility of the film after each treatment (equation 4.2).
\[ \frac{1}{\rho} = qn \mu \]  

(4.2)

The effect of increasing the oxidation temperature is to increase the film resistance\cite{55}. Although the films have already been treated with EDT prior to annealing, a post annealing treatment increases the resistivity significantly for all of the films\cite{70}. This is attributed to better surface passivation which reduces the number of acceptor states lying near the valence band. It is worth emphasizing that this is not, a priori, the obvious effect of surface passivation. As discussed in the introduction on a-Si, passivation of mid gap states generally moves the Fermi level nearer to the conduction or valence band for the n or p type material respectively and increases conductivity.

![Figure 4-3: Effect of air annealing and EDT re-treatment on film resistivity.](image)

4.2.2 Measurement of the Mobility using a Field Effect Transistor

The resistivity is determined by the carrier density and the mobility. The mobility can be measured using a field effect transistor\cite{55}. Figure 4-4(a) shows the source drain current \( (I_{ds}) \) as a function of gate bias \( (V_g) \). The mobility extracted for each channel length is shown in the inset, and the mobilities are consistent across the device. For the sample studied which was annealed at 60 C and did not undergo re-treatment, the mobility is \( \approx 10^{-4} \text{ cm}^2/\text{Vs} \). This is consistent with mobility of CdTe\cite{14} and literature values for PbS with EDT treatment\cite{55}.
Figure 4-4: Extraction of the mobility of a PbS QD film using a field effect transistor. (a) $I_{ds}$ is measured as a function of $V_g$ (black circles). The observed hysteresis indicates trapping in the film. A portion of the sweep from 0 to -20 $V_g$ (red circles) is fit to extract the mobility (red line). The inset shows that the mobility calculated for different channel lengths is consistent.

Considerable hysteresis is observed between the sweep up and sweep back. This is attributed to trapping in the film. One explanation of the hysteresis is that when the gate is biased to induce holes into the film, the holes initially enter into the conduction band and are highly mobile. After a period of time, these settle to the Fermi level and begin to occupy traps, reducing the effective mobility as given by equation 4.3.

$$\mu_{eff} = \mu_0 \exp\left(-\frac{E_c - E_f}{kT}\right)$$

(4.3)

Therefore the mobility measured may be between the no trap limit and the effective mobility limit, and may be higher than the mobility under dark equilibrium conditions. However, the mobility measurement still serves as a decent estimate and provides a comparison between treatments.

### 4.2.3 Effect of Oxidation and Treatment on the $\mu T$ product.

For photoconductors with an injecting contact for the majority carrier, the photocurrent is given by equation 4.4[62].
In equation 4.4, $F$ is the photon flux per cm$^2$, $A_d$ is the detector active area, and $[1 - \exp(-\alpha H)]$ is the absorption of the detector at the wavelength of excitation where $\alpha$ is a measure of the extinction coefficient and $H$ is the film height. $G$ is the photoconductive gain as defined by equation 4.5.

$$G = \frac{\mu \tau V}{L^2}$$

The internal quantum efficiency (IQE) is equal to the gain by definition. The internal quantum efficiency can calculated if the absorption of the film is known. While finding the absorption of the film with high accuracy requires measuring the transmission and reflection of the film accurately, an approximate value for the absorption can be obtained from the transmission spectrum and is sufficiently accurate for the scientific analysis here.

Equation 4.5 predicts a $L^{-2}$ dependence of the internal quantum efficiency. This dependence is clearly observed in figure 4-5. From the fit we obtain a value for the $\mu \tau$ product. This gives an intrinsic measure of the photoconductive properties of the film after each treatment similar to the resistivity measurement of the dark current properties. Figure 4-5 gives the $\mu \tau$ product as a function of the oxidation and EDT re-treatment.

### 4.2.4 Photoaction Spectrum

The transmission spectra for annealed films are shown in figure 4-6(a). Figure 4-6(b) shows the same data with the background scattering subtracted. A clear blue shift in the first absorption feature is observed with increasing annealing temperature. This is associated with oxidation of the outer layers of the PbS QD core. The effects of oxidation on PbS QDs has been studied by XPS, and formation of PbO as well as PbSO$_3$ and PbSO$_4$ has been observed[55, 70] The photo-action spectrum of the device annealed at 60 C is shown in figure 4-6(c). The photo action response follows the
Figure 4-5: (a) Dependence of the EQE on channel length. Circles are data extracted from the slope of the EQE versus voltage curve for each channel length. The line a fit to equation 4.5 and demonstrates the $L^{-2}$ channel length dependence. (b) The $\mu\tau$ product for different treatment conditions.

absorption spectrum of the quantum dot film as expected.

Figure 4-6: (a) Transmission spectra of films treated at 60 C (green line), 80 C (red line) and 100 C (light blue line) are compared to the spectrum of a film without oxygen exposure (dark blue line). (b) Spectra from (a) with scattering background subtracted. (c) Photoaction spectrum of sample annealed at 60 C.

4.2.5 Bandwidth

Figure 4-7 shows the effect of voltage, channel length, treatment and excitation intensity on the bandwidth of the device. Figure 4-7(a) shows that from 0.1 V to 10 V bias, the bandwidth of the device is unchanged. Therefore the device is not in the gain bandwidth limit where an increase in gain would be associated with a decrease in the bandwidth. The slight increase in the bandwidth at 100 V is attributed to the electron reaching the contacts at high voltage. Similarly, the bandwidth does not
depend on the channel length as shown in figure 4-7(b). While there is some variation in the bandwidth, there is no consistent trend as demonstrated by the inset. This indicates that recombination occurs in the bulk, not at the electrodes.

Figure 4-7: (a) Dependence of the bandwidth on bias voltage. (b) Effect of channel length on bandwidth. (c) Effect of treatment on bandwidth. Re-treated samples have a clear increase in bandwidth. (d) Intensity dependence of the bandwidth.

Figure 4-7(c) shows the effect of treatment on the bandwidth. While the annealing temperature does not have a clear effect for the samples that did not undergo re-treatment, the bandwidth is clearly higher for the treated samples and the bandwidth increases slight with increasing annealing temperature. The increase in bandwidth may be associated with a reduction in shallow trap states. This is consistent with a reduction in the dark current due to surface passivation.

The intensity dependence of the bandwidth is shown in figure 4-7(d). The band-
width decreases with decreasing excitation intensity until it reaches a constant value. This is shown in figure 4-8, where the bandwidth is plotted against the relative excitation intensity. This behaviour is a result of the increasing amount of bimolecular carrier recombination at higher excitation levels\cite{38}. Equation 4.6 gives the rate of change in the hole density due to photo generation, monomolecular decay and bimolecular decay.

\[
\frac{dn}{dt} = F - (N_t + p)pb
\]  

(4.6)

Solving for the steady state gives equation 4.7.

\[
p = \frac{N_t}{2} \sqrt{1 + \frac{4F}{N_t^2b}} - 1
\]  

(4.7)

The hole lifetime is defined by the relation \(\tau_h = p/F\). Since the bandwidth should be inversely proportional to the lifetime, we can express the relationship between the bandwidth and the excitation rate by equation 4.8.

\[
f_c \propto \frac{2}{N_t} \frac{F}{\sqrt{1 + \frac{4F}{N_t^2b}} - 1}
\]  

(4.8)
For high excitation rates where $4F/Nb^2 \ll 1$, this reduces to $f_c \propto \sqrt{bF}$. At low excitation, the bandwidth is constant. The measured bandwidth data in figure 4-8 is fit well by equation 4.8. The inverse of the bandwidth is expected to be proportional to the external quantum efficiency, and this relationship is observed (figure 4-8(b)).

4.2.6 Noise

Although there are a variety of models that predict the magnitude of noise present in a specific system, these models calculate the ideal limit and usually underestimate the noise. The only way to know the magnitude of the noise is to directly measure it. Since the fluctuations of the current are much smaller than the current itself, noise measurements can be difficult to make experimentally. The calibration of our measurement apparatus is discussed in the experimental section.

In noise analysis, the events that generate both the dark current and photocurrent are assumed to follow Poisson statistics. The magnitude of the standard deviation, $\Delta N$, for a random Poisson process is given by the equation 4.9 where $N$ is the event rate and $\Delta f$ is the bandwidth over which the noise is integrated[71].

$$\Delta N^2 = 2N\Delta f$$

(4.9)

The fluctuation in current due to excitation of free carriers is given by equation 4.10, where $i_n$ is the magnitude of the fluctuation, $F$ is the carrier generation rate, and $\alpha$ is the contribution per an event[71].

$$i_n^2 = 2F\alpha^2\Delta f$$

(4.10)

For a photovoltaic detector, an event is typically photoexcitation by incident light or thermionic emission over the p-n barrier. In either case, the contribution to the current is a single electron-hole pair flowing through the circuit. Recombine occurs at the contacts and the gain is unity. Since the gain is unity, the contribution per event is $q$, the electron charge, and $\alpha = q$. Substituting into equation 4.10, this gives the common shot noise equation (equation 4.11).
\[ i_n = \sqrt{2qI\Delta f} \]  \hfill (4.11)

For a photoconductor, the contribution is equal to the gain of the device multiplied by the electron charge, \( \alpha = eG \), since the detector counts \( G \) electrons passing through the circuit per event. In addition, since both the generation and the recombination are random events, the total noise is increased by a factor of \( \sqrt{2} \). The generation-recombination (GR) noise is given by equation 4.12.

\[ i_n = \sqrt{4qGI\Delta f} \]  \hfill (4.12)

The shot noise and GR noise equations predict a flat noise spectrum, where the amount of noise is the same at all frequencies (white noise). The noise spectrum for a PbS QD film in the dark is shown in figure 4-9. A clear frequency dependence is observed which can be fit well by the power law decay in equation 4.13 where \( C \) is a constant.

\[ i_n = \frac{C}{f^p} \]  \hfill (4.13)

The value of \( p \) can vary but is typically close to 0.5. This type of noise is frequently observed and is known as 1/f noise. While there is no universally accepted theory for the source of 1/f noise, it is commonly associated with a variance in the carrier lifetimes, grain boundaries and other types of disorder. There is certainly a great deal of disorder in the PbS QD system. Since the 1/f noise reduces with increasing frequency, at high frequency it will fall below the generation recombination noise. We do not observe this up to 10 kHz as evident in figure 4-9(a).

Equations 4.11 and 4.12 above predict very different voltage and channel length dependences of the scaled noise current, \( i_n/\sqrt{I} \). For the shot noise case, where noise is generated by events with unity gain, the scaled noise current is constant. Expanding equation 4.12 shows the voltage and channel length dependence for generation recombination noise.
Figure 4-9: (a) Dark current noise density as a function of frequency up to 10 kHz. (b) Dark current noise under different bias conditions (solid colored lines). The data is fitted to $C/f^0.5$ (black lines). Dashed lines denote the shot noise limit.

$$\frac{i_n}{\sqrt{I}} = \sqrt{4q\mu t} \Delta f \sqrt{\frac{V}{L}}$$  \hspace{1cm} (4.14)

Figure 4-10 shows the channel length and voltage dependence of the magnitude of 1/f noise. A good fit to the generation-recombination model is observed. After determining this relationship, I came across the standard relationship between the current and noise current used to describe 1/f noise. This is expressed by the Hooge relation in equation 4.15, where $N_C$ is the carrier density and $\alpha_H$ is known as the Hooge parameter[72].

$$\left(\frac{i_n}{I}\right)^2 = \frac{\alpha_H \Delta f}{N_C f}$$  \hspace{1cm} (4.15)

The Hooge parameter is a dimensionless unit. Although it was originally derived for a particular set of physics concerning crystalline semiconductors, it is widely used as an empirical constant which will depend on the physics of a particular system.
Using the relationship \( I = qN_C\mu V/L^2 \) equation 4.15 can be rearranged to express the observed voltage and channel length dependence.

\[
\frac{i_n}{\sqrt{f}} = \sqrt{\alpha_h} \sqrt{4q\mu \frac{\sqrt{V}}{L}} \sqrt{\frac{\Delta f}{f}} \tag{4.16}
\]

The voltage and channel length dependence in the Hooge equation are the same as observed in figure 4-10.

If we can measure the noise current as a function of the carrier density, we can test the relationship in equation 4.15. Figure 4-11(a) shows the noise under illumination by a tungsten lamp. The tungsten lamp is used as a shot noise limited photon source. Clear 1/f behaviour is observed in the photocurrent noise. Figure 4-11(b) shows a plot of \( i_n/\sqrt{f} \) for different illumination intensities. The relationship is constant at all excitation frequencies. Figure 4-11(c) shows the intensity dependence of the DC current on the excitation intensity. A bimolecular recombination mechanism dominates such that \( N_C \propto \sqrt{F} \). This suggests that a plot of \( (i_n/I)^2 f \) versus \( 1/\sqrt{F} \) should have a linear dependence. A linear relationship is indeed observed (figure 4-11(d)). More work remains to be done to compare the quantity of the noise for different samples and to understand the implications of the Hooge parameter from a theoretical perspective.

Finally, we can rearrange the Hooge equation in a manner that is more useful for the discussion of detectivity below. Using \( I = qN_C\mu V/L^2 \), equation 4.15 can be expressed as 4.17.
\[ i_n = \frac{q \mu V}{L^2} \sqrt{\alpha H N_C} \sqrt{\frac{\Delta f}{f}} \]  

(4.17)

Figure 4-11: (a) Noise current for different levels of photoexcitation. (b) \( i_n/\sqrt{I} \) for different excitation intensities. (c) Intensity dependence of the photocurrent showing bimolecular carrier recombination. (d) Comparison of \( (i_n/I)^2 \) for different excitation intensities. A good fit to a carrier density determined by bimolecular recombination is observed.

4.2.7 Detectivity

The detectivity is given by equation 4.18[73]. It is the accepted figure of merit for detector performance and is normalized for the device area \( A_d \) and the noise spectral bandwidth \( \Delta f \). It is related to the noise equivalent power (NEP) as shown in equation 4.18. The noise equivalent power gives a measure of the photon flux on the detector which will generate a signal equal to the noise. This is understood to be the minimum photon flux that can be detected.
As written, equation 4.18 suggests that $D^*$ is expressible as a single number for a particular detector, which is not the case. As discussed above, the responsivity changes with operation frequency, excitation intensity, voltage and channel length. The noise is a function of operation frequency, voltage and channel length.

From the analysis above, we can expand the equation for detectivity as a function of channel length and operation voltage. The relationship between the responsivity and the external quantum efficiency is $R = E\text{QE}(q\lambda)/(hc)$. We can expand the responsivity using the results above as shown in equation 4.19, where $BW(f)$ takes into account the decrease in the responsivity with increasing frequency.

$$R = \frac{[1 - \exp(\alpha H)]\mu \tau V}{L^2}BW(f)\frac{q\lambda}{hc}$$  \hspace{1cm} (4.19)

Equation 4.17 gives an expression for the noise current in terms of the voltage and channel length as well. This equation is expressed by equation 4.20 in terms of the carrier density $n_C$ using $N_C = n_C(L\cdot W\cdot H)$ where $L$ is the distance between electrodes, $H$ is the height and $W$ is the electrode length.

$$i_n = \frac{q\mu V}{L^2}\sqrt{\alpha_H n_C}\sqrt{L\cdot W\cdot H\sqrt{\frac{\Delta f}{f}}}$$  \hspace{1cm} (4.20)

For the lateral devices used here, the device area is given by $A_d = L\cdot W$. Substituting equations 4.19 and 4.20 into the detectivity equation gives equation 4.21.

$$D^* = \left(\frac{\lambda}{hc}\right)\left(1 - \exp(-\alpha H)\right)\left(BW(f)\sqrt{f}\right)\left(\frac{\tau}{\alpha_H n_C}\right)$$  \hspace{1cm} (4.21)

Equation 4.21 has many components, but each component expresses a simple relationship. The first thing to note is that the voltage, channel length and mobility have cancelled out. In the linear regime, the detectivity is independent of these parameters. The relation $\lambda/hc$ converts the wavelength dependent responsivity into the physically relevant external quantum efficiency. The term $[1 - \exp(-\alpha H)]/H$
expresses the fact that a thicker film will absorb more light, increasing $R$, but will also have more dark current, increasing the noise. The ideal height can be calculated using the extinction coefficient for the film. The term $BW(f)\sqrt{f}$ relates the decrease in noise as a function of increasing frequency with the decrease in the bandwidth at higher frequencies. This will determine the ideal frequency of operation for the device, which will generally be near the roll off frequency. Finally, $\tau/\alpha_hn_C$ expresses two fundamental characteristics of the film. $\tau$ gives a measure of the photosensitivity of the film, and $\alpha_hn_C$ expresses how much noise is due to dark current. If the dark current carrier density is reduced or the photocurrent lifetime is increased, the detectivity will increase.

Figure 4-12 provides experimental verification of these results. The detectivity is shown as a function of operating frequency, the channel length, the intensity of excitation, and the applied bias. As a function of frequency, the detectivity initially increases since the magnitude of the $1/f$ noise reduces with frequency. Near the corner frequency, the roll off goes as $\approx f^{-1/2}$. The result is that the decrease in responsivity and decrease in noise nearly cancel out over this region and the detectivity spectrum is flat. At higher frequencies, the roll off will eventually dominate and the detectivity will decrease. Figure 4-12(b) shows the detectivity as a function of the excitation intensity. At high excitation intensities, bimolecular recombination reduces the lifetime and the detectivity decreases. The dependence of the detectivity on channel length and bias is expected to be constant. This is observed for the channel length dependence, but a weak dependence on voltage is observed. This is readily understood considering the discussion in the chapter 1 on voltage assisted thermal activation. The voltages applied in figure 4-12(d) are well beyond the linear regime. At high bias, the carrier density is increased which results in a decrease in the detectivity. This effect is minor however and will not effect the operation in the linear current voltage regime.
Figure 4-12: Detectivity as a function of frequency, channel length, excitation intensity and voltage. (a) Detectivity as a function of illumination. Black line is experimental data. Red line uses a $1/f$ fit to the noise combined with the measured bandwidth data to give an empirical fit. (b) Detectivity as a function of the intensity of illumination. At high intensities, the decreasing lifetime due to bimolecular recombination results in a decrease in detectivity. (c) Detectivity as a function of channel length. No dependence is observed. (d) The detectivity as a function of voltage. At low voltages, the detectivity is independent of voltage. At higher voltages where the IV curve is non linear, the voltage assisted activation mechanism discussed in chapter 1 results in an increase in the carrier density.

4.3 Conclusion

The final step in this project will be incorporation of our QD film in an infrared imaging camera. While we are not at this stage yet, we have presented a method to control the resistivity of our PbS QD films to facilitate incorporation and hopefully will realize our final objective shortly. In the meantime, we have undertaken a thorough study of the responsivity and noise current in our PbS QD films. We look forward to taking the analysis presented here and adding on a quantitative analysis of the effects of oxidation and treatment in the future.
4.4 Appendix

4.4.1 Capacitance, Integration Time, and Pixel Resistance

Consider a capacitor with capacitance \( C \) which has an initial charge \( Q_0 \) in parallel with a resistor with resistance \( R_d \) as depicted in figure 4-2(d). The charge on the capacitor will flow through the resistor over time. The rate of change of the charge \( Q(t) \) is given by

\[
\frac{dQ}{dt} = -I = \frac{V}{R} = -\frac{Q}{RC}
\]  

Solving for \( Q(t) \) gives equation 4.23.

\[
Q(t) = Q_0 \exp(-\frac{t}{RC})
\]  

The time after which one half of the charge will be depleted (\( \tau \)) is given by equation 4.24.

\[
\tau = RC \ln(2)
\]  

The larger the capacitance, the smaller the resistance can be. The shorter the integration time, the smaller the resistance can be as well.

4.4.2 Film Resistivity

For an annular pixel as depicted in figure 4-1, the resistance is calculated from the resistivity (\( \rho \)) by equation 4.25.

\[
R = \rho \frac{\log B_e}{2\pi D}
\]  

The resistance is determined by the integration time and the capacitance as discussed above. If the target resistance is \( \approx 100 \) G\( \Omega \) and we want a \( \approx 100 \) nm film to absorb the incoming light, then the desired resistivity is given by equation 4.26.
\[
\frac{(10^{11}\Omega)(2\pi)(5 \cdot 10^{-7})}{\ln(7.5/3.5)} = \rho \approx 100\Omega/m
\]  

(4.26)

### 4.4.3 Linear Region

Figure 4-13 shows typical linear dark current versus voltage and photocurrent versus voltage curves. All current-voltage curves measured where linear for fields below 3 kV/cm.

![Figure 4-13: (a) Dark current versus voltage at low field displaying a typical linear relationship (b) Photocurrent versus voltage at low field displaying a typical linear relationship](image)

### 4.4.4 Noise Measurements

Noise measurements are made using an Ithaco 1211 amplifier to convert the noise current to a voltage which is measured by a Stanford Research System 785 dynamic signal analyser. Noise measurements are magnitude average to reduce the error in the measurements and all results are reported per \( \sqrt{Hz} \). The measurement system was tested against a series of resistors as shown in figure 4-14. The measured noise spectrum is flat as expected for Johnson noise, and the magnitude of the measured noise agrees with the theoretical prediction (figure 4-14(b)).

The intensity dependence of the noise is measured using a shot noise limited photon source from a tungsten lamp. The white light is passed through a short pass filter and a long pass filter to limit illumination to the visible region. The illumination is modulated with an absorptive ND filter.
4.4.5 Photocurrent

Bandwidth and intensity dependence measurements are done using a 660 nm diode laser modulated in a square wave pattern by an acousto-optic modulator. The photocurrent is measured with a lock in amplifier (Stanford Research Systems 830). For the photo-action measurements, the excitation source is the output of a monochromator chopped using a mechanical chopper and passed through long pass filters to remove overtones. The intensity of the light on the device is measured using calibrated Si and Ge detectors (Newport 818-UV and 818-IR).
Chapter 5

Luminescent Down Conversion
with Quantum Dots

5.1 Preface

This chapter presents an application of quantum dots to solve an important engineering challenge: dual band detection. Although I believe quantum dots (QDs) are uniquely suited for this application, this technology would not have been developed without the input of the Institute of Soldiers and Nanotechnology and Frank Jaworski from Raytheon. Without this collaboration, we would not have been aware of the need for UV-NIR and NIR-MWIR dual band detection and this important application of QDs would not have been developed. We have had the advantage of receiving constant feedback on our design throughout the process, and I hope that the results presented in this chapter will ultimately find a real world application.

This work is currently in preparation for submission. I would like to acknowledge Frank Jaworski again, who has provided guidance throughout the project from inception. Jen Scherer has adopted this project and quickly increased our device efficiencies, and Nosipho Moloto has characterized the properties of our down conversion layer.
5.2 Introduction

P-n junction photodetectors are designed to operate with high efficiency across a specific band of the electromagnetic spectrum. Photons with energy below the detector band gap are not absorbed by the material, and photons with energy far greater than the band gap are absorbed near the surface of the detector and are not collected efficiently [74]. For a number of defence and civilian applications the capability to detect two or more bands simultaneously with a single imaging system is of interest [75, 76, 77, 78]. Fabrication of an imaging camera with two or more alternating detector elements sensitive to different spectral bands is technically challenging and costly [69]. An alternative is luminescent down conversion (LDC) of photons with energy above the detector band using fluorescent dyes [74, 79] or colloidal quantum dots (QDs) [80, 81]. In this method, a layer incorporating the fluorophore is deposited above the detector and absorbs high energy photons. These relax to the HOMO-LUMO level of the emitter and are re-emitted in the detector band. This method has been demonstrated for UV-Vis down conversion to enhance solar cell efficiency using organic dyes and is also known as luminescent down shifting (LDS) [74, 79]. In this chapter we demonstrate the application of colloidal quantum dots to sensitise short wavelength infrared (SWIR) detectors to ultraviolet light. UV-IR dual band detectors have applications in flame identification, muzzle flash identification, communications and cover tagging [75, 76]. We demonstrate that the unique absorption profile and high quantum yield (QY) of QDs make these particles ideal candidates for LDC emitters in UV-IR applications and dual band detectors in general.

5.3 Design

Figure 5-1 depicts the function of a QD based UV-IR LDC detector. Infrared light with wavelengths in the detector band is collected with high efficiency by the bare detector. For the InGaAs SWIR detectors used in this study, the detector band is from 950 nm to 1650 nm. Higher energy light is absorbed in near the detector surface,
not in the active region of the p-n junction detector. Surface states and a low minority carrier diffusion length result in a low internal quantum efficiency and therefore poor sensitivity to visible and ultraviolet light[74, 75]. In the LDC detector geometry, a layer containing luminescent QDs is deposited on the bare detector. Ultraviolet light is absorbed by the QDs and re-emitted in the infrared region where it is collected with high efficiency by the InGaAs detector. The LDC layer should be transparent across the detector band to avoid decreasing the infrared sensitivity. Unlike organic dyes, QDs absorb more strongly to the blue of HOMO-LUMO transition than at the HOMO-LUMO transition. By selecting the appropriate concentration of QDs, the LDC layer will absorb strongly in the ultraviolet while being nearly transparent in the infrared.

![Diagram](image)

Figure 5-1: Cartoon of a QD sensitized UV-IR luminescent downconverter compared to a bare detector. Infrared light incident on the bare detector (a) is collected in the active region of the detector (gray box). Ultraviolet light (b) is collected near the surface of the detector (yellow box) at low efficiency. With the addition of the LDC layer, ultraviolet light (c) is absorbed by the QDs and re-emitted in the infrared where it is collected in the active region of the detector. Due to the absorption profile of the QDs, the LDC layer absorbs most of the UV light, but is nearly transparent to infrared light (d).

To increase the quantum yield of the LDC layer, the QDs are suspended in a polymer matrix. The polymer serves to increase the interparticle distance between the QDs which reduces fluorescence resonant energy transfer (FRET) between QDs. FRET transfer in QD films can reduce the overall film QY via transfer of excitons from QDs with high QY to QDs with low QY [20, 82]. By embedding the QDs in a photoresist such as poly(methyl methacrylate) (PMMA), pixelation of the detector
can be readily achieved[83]. Efficient LDC layers were made with QDs dispersed in PMMA, poly(acrylic acid) (PAA) and poly(vinyl butyral) (PVB). The loading fraction by volume of QDs in the polymer/QD LDC layer is determined by optical absorption, the extinction coefficient of the quantum dots, and the film height (see experimental)[84].

5.4 Results

5.4.1 EQE

The absorption and emission spectra of the QDs in solution are shown in figure 5-2 overlaid with the external quantum efficiency of an InGaAs short wavelength infrared (SWIR) detector. The size of the QD core is chosen so that the emission overlaps with the high efficiency region of the SWIR detector. The quantum yield of the QDs in solution is 40%. In a thin film without dispersion in a polymer the QY is reduced to 10% due to FRET. Embedded in PAA, the QY of the QDs is 30%. Since this work was done, we have achieved quantum yields of over 40% with QDs embedded in PMMA.

Figure 5-3 shows the external quantum efficiency (EQE) spectrum of an InGaAs photodiode before and after deposition of a LDC layer with PbS/CdS QDs embedded in PAA. The EQE spectrum of the QD LDC photodiode clearly show an enhancement of the EQE in the visible and ultraviolet region after deposition of the QDs. Minimal decrease in the EQE of the detector in the infrared region is observed. The data is fit using the solution phase absorption profile of the QDs and the methods discussed below.

5.4.2 Bandwidth

The bandwidth of a detector determines the maximum frame rate for imaging and the maximum frequency for communication. Photons not absorbed by the LDC layer will be detected at the bandwidth of the bare detector. The bandwidth of the LDC
Figure 5-2: The absorption (black line) and emission (red line) spectra of a PbS/CdS polymer film is shown compared to the EQE of a characteristic InGaAs SWIR detector (blue line).

Figure 5-3: The efficiency of an InGaAs detector before (black line) and after addition of a PbS/CdS based LDC layer (red line). The data is fitted using the model discussed below (blue line), and the scaled absorption profile of the PbS/CdS QDs is shown (blue dashed line).

layer will be dominated by the delay between absorption and re-emission of photons by the QD, which is determined by the photoluminescent (PL) lifetime, \( \tau_{PL} \). The frequency response associated with a single exponential decay is given by equation 5.1. The bandwidth is equal to the corner frequency, \( f_c = \frac{1}{2\pi \tau_{PL}} \).

\[
\Omega_L (f) = \frac{1}{\sqrt{1 + (2\pi \tau_{PL} f)^2}} = \frac{1}{\sqrt{1 + \left(\frac{f}{f_c}\right)^2}}
\] (5.1)
Fluorescent dye lifetimes are typical on the order of \( \approx 1-5 \text{ ns} \)\cite{85}, while quantum dot lifetimes vary from \( \approx 25 \text{ ns} \) for CdSe\cite{86} to \( \approx 1 \mu \text{s} \) for PbS and PbSe QDs\cite{87, 88}. The longer lifetime for lead chalcogenide QDs compared to CdSe QDs has been attributed to the higher dielectric constant\cite{87} and higher 1S state degeneracy\cite{88} in PbS and PbSe.

Figure 5-4 (a) shows the measured bandwidth of a LDC detector made with PbS/CdS QDs in a PAA matrix under UV excitation and IR excitation. The bandwidth of the underlying InGaAs photodiode is rated at 35 MHz and the response of the bare detector to UV and IR light is flat to 1 MHz. The LDC detector IR response is flat below 1 MHz as expected since IR photons are not absorbed in the LDC layer. In contrast, the LDC detector UV response rolls off at 150 kHz and the lifetime extracted from equation 5.1 is 1.1 \( \mu \text{s} \). This is consistent with the bandwidth of PbS NCs which is typically on the order of 1 \( \mu \text{s} \). The bandwidth of the PbS QD based LDC is more than sufficient for most imaging applications. For optical communications, a higher LDC bandwidth can be achieved with InAs QDs. Figure 5-4 (b) shows the photoluminescent decay of InAs/CdZnSe QDs in a PAA film. The measured lifetime is \( \tau_{PL} = 10 \text{ ns} \). The Fourier transform of the transient photoluminescence decay is shown in figure 5-4 (c), and the calculated bandwidth is 8 MHz. The Fourier transform is calculated as \( \hat{f}(v) = |\int_{-\infty}^{\infty} f(t)e^{-2\pi i vt} \, dt|^2 \).

Figure 5-4: (a) Bandwidth of a PbS/CdS based LDC detector under UV illumination. The detector bandwidth is 150 kHz, corresponding to a lifetime of 1.1 \( \mu \text{s} \). (b) Transient photoluminescence measurement of InAs/CdZnSe NCs with a 10 ns lifetime. (c) Fourier transform of the lifetime data in plot (b) giving the expected bandwidth of an InAs based LDC detector.
5.5 Theory and Discussion

The EQE of the LDC detector at a specific wavelength $\eta_C(\lambda)$, is given by equation 5.2 in terms of the absorption of the LDC layer, $A(\lambda)$, the efficiency of the LDC layer, $\phi_L$, the maximum EQE of the bare detector, $max(\eta_B)$, and the relative EQE of the bare detector $\phi_B(\lambda) = \eta_B(\lambda)/max(\eta_B)$.

$$\eta_C(\lambda) = [(1 - A(\lambda)) \phi_B(\lambda) + A(\lambda) \phi_L] max(\eta_B)$$  \hspace{1cm} \text{(5.2)}

Equation 5.3 gives $\phi_L$ as a function of the quantum yield of the fluorophore, $QY$, the emission overlap integral $\Theta_{Em}$, and the collection efficiency $CE$.

$$\phi_L = QY \cdot \Theta_{Em} \cdot CE$$ \hspace{1cm} \text{(5.3)}

The emission overlap integral $\Theta_{Em}$ characterizes the average efficiency with which a photon of emitted light incident on the detector is detected. It is expressed in terms of the normalized emission profile of the fluorophore $P_{em}(\lambda)$ and the normalized efficiency of the bare detector by equation 5.4. For fluorophores with emission overlapping the detector band, $\Theta_{Em}$ will be near unity.

$$\Theta_{Em} = \int P_{em}(\lambda) \phi_B d\lambda$$ \hspace{1cm} \text{(5.4)}

The collection efficiency is the fraction of photons emitted by the fluorophores that are ultimately incident on detector. The main $CE$ loss mechanisms are transmission across the LDC layer/air interface and re-absorption by the emitter. For simplicity, we consider the case of zero re-absorption of photons in the LDC layer and model the transmission losses using the Fresnel equation (see experimental). The collection efficiency will depend on the index of refraction of the LDC layer. As the QD loading fraction increases, the index of the LDC layer increases from the index of the polymer to the index of the QD film[89] and the collection efficiency will increase. For pure PMMA, the collection efficiency is calculated to be 72% for $n=1.4$. For a 5% QD composition by volume we find $n=1.5$ by ellipsometry, and the collection efficiency is...
calculated to be 77%.

Equations 5.2-5.4 present a simple model for the wavelength dependent efficiency of the LDC detector. In particular, while the quantum yield and collection efficiency are difficult to measure experimentally with high accuracy, the remaining inputs are readily measured or calculated. Figure 5-5 compares the fits (light lines) to the experimental data (dark lines). The fitting is done by varying the magnitude of the solution phase absorption spectra (dotted lines) and the $CE \cdot QY$ product. Highly absorbing LDC layers, thicker than would be used in a practical device, are shown to demonstrate that the model can predict both the down conversion band enhancement as well as the detector band degradation.

![Figure 5-5](image)

Figure 5-5: (a) Efficiency of a bare InGaAs detector (black line) is compared to the efficiency after adding LDC layers with medium (blue lines) and high (red lines) concentrations of PbS/CdS QDs. These concentrations are higher than practical and are presented only to demonstrate the accuracy of the fit (dashed lines). The light red and blue lines are the fitted absorption profiles to the dark red and blue lines respectively.

5.5.1 Detector Band Transparency, $T_A(\lambda_{DC})$

The quantum yield and emission overlap integral provide figures of merit for the emission properties of the fluorophore. Figure 5-6 demonstrates the effect of different absorption profiles on the detector efficiency. In order for organic dyes to absorb strongly in the UV region, the concentration must be increased to the point where
absorption at the HOMO-LUMO transition saturates. Absorption by the LDC layer in the detector band will degrade the detector band performance and should be minimized while maintaining a high emission overlap integral and strong absorption in the down conversion band. We propose a figure of merit for the absorption profile of a fluorophore that characterizes its transparency in the detector band for a given absorption in the down conversion band. $T_A(\lambda_{DC})$, the detector band transparency, is the fraction of photons in the detector region that pass through the LDC layer for a given average absorption, $A$, in the down conversion band. The down conversion band wavelengths are denoted $\lambda_{DC}$. $T_A(\lambda_{DC})$ can be calculated from the absorption spectrum of the fluorophore, and the EQE spectrum of the bare detector (see experimental). For example, in the simulation shown in figure 5-6(a) and 5-6 (b), both the QD and dye LDC layers absorb 95% of the incoming light between 300 and 400 nm. The QD LDC layer maintains near complete SWIR transparency, while the dye LDC layer absorbs strongly in the detector band, leading to a decrease in SWIR sensitivity. $T_{95}(300-400)$ is 99% for the PbS/CdS QDs and 63% for the Q Switch 5 dye (Exciton Dye Source).

A high detector band transparency can be accomplished by a large wavelength shift between the absorption and emission, i.e. a large Stokes shift, which is often the goal when using organic dyes[90]. For QDs, a large effective Stokes shift may be obtained using doped dots[91] or using a type II structure[16]. FRET may also be employed to transfer excitons from a higher band gap materials to the emitting fluorophore, and a variety of FRET based dye-dye[90], QD-QD[20], QD-dye[92] and dye-QD[93] constructs exist. Alternatively, for QDs the extinction coefficient rapidly increases with decreasing wavelength unlike organic dyes which have a peak in the oscillator strength at the HOMO-LUMO transition. The difference in down conversion band and detector band absorption can be used to create an LDC layer that is highly absorptive in the down conversion band and highly transparent in the detector band without requiring a large Stokes shift. This effect can be increased by the growth of a core/shell structure such as for PbS/CdS where the shell material does not absorb in the detector band. The shell serves as an optical antenna to absorb down conversion
Figure 5-6: (a) Calculated efficiency of a LDC detector based on the absorption profile (dashed black line) of the PbS/CdS QDs used in the above study. The performance as a function of the QD quantum yield (colored lines) is compared to the bare detector (solid black line). A collection efficiency of 77% is assumed, and the absorption is set such that 95% of the incoming light is absorbed between 300 and 400 nm. (b) An equivalent calculation is done for Q Switch 5, a common SWIR fluorescent dye. Since the strongest absorption is at the HOMO-LUMO transition, the dye based LDC layer absorbs nearly 100% of the incoming light in across much of the detector band leading to a loss in SWIR performance.

band photons and transfer the exciton to the core material.

Figure 5-7 presents figure of merit values for several SWIR emitting dyes and QDs. Red squares indicate the critical regions of poor performance that limit the application of the organic dyes for UV-IR downconversion, while green squares indicate near ideal performance. The current limitation for QD based UV-IR downconverters is clearly the quantum yield. Figure 5-6(a) shows the expected efficiencies obtainable for different values of the QD quantum yield. Given the recent advances in high QY visibly emitting QDs where QY values above 90% are obtained[94], it is plausible that QD based UV-IR LDC detectors with down conversion band efficiencies greater than 60% will be achievable using the architecture presented here as synthetic progress is made with high QY SWIR emitting QDs.
<table>
<thead>
<tr>
<th>Fluorophore</th>
<th>QY [1]</th>
<th>Θ_{em}</th>
<th>T_{spectral} [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS/CdS QDs</td>
<td>55%</td>
<td>0.97</td>
<td>0.99</td>
</tr>
<tr>
<td>Q switch 5</td>
<td>0.05%</td>
<td>0.97</td>
<td>0.63</td>
</tr>
<tr>
<td>Cardiogreen</td>
<td>13%</td>
<td>0.38</td>
<td>0.99</td>
</tr>
</tbody>
</table>

[1] Solution QY
[2] λ_{exc}=300-400 nm

Figure 5-7: Figure of merit values for several SWIR emitting fluorophores. Red boxes indicate critical areas of poor performance and green boxes indicate near ideal performance.

5.5.2 Cross talk

Optical cross talk occurs when light directed towards a given pixel by the imaging optics ultimately strikes a different pixel and leads to a loss in imaging resolution [95, 96]. For a bare detector, optical cross talk results from reflection and scattering. Here we consider the increase in optical cross talk due to absorption and remission of photons in the LDC layer. Light absorbed in the LDC layer is re-emitted isotropically and may travel a significant distance away from the spot of emission before being detected. However, light that is not absorbed in the LDC layer will be detected with the same imaging resolution as the bare detector. By selecting a material with a high detector band transparency, as is the case for QD based UV-IR LDC detectors, minimal loss of resolution will occur over the detector band.

Optical cross talk can be characterized by the radial probability distribution function (PDF) of photons striking the detector at distance r from an emitter at height h above the detector as depicted in figure 5-8(a). The film height is given by H. We present optical cross talk calculations for two ideal cases which represent the limits of high absorption and low absorption of incident light by the film. For simplicity, re-absorption of emitted light in the LDC layer is assumed to be negligible and complete reflection at the LDC/air interface is assumed. A more detailed calculation arrives at similar results (see experimental).

Case 1: If the extinction coefficient of the LDC layer at the incident wavelength is small, the generation of excited states will be nearly uniform throughout the LDC layer, and the probability distribution function is given by equation 5.5. Case 2: If
the extinction coefficient at the wavelength of the incident light is large, then the light will be collected near the air/LDC layer interface, and the probability distribution function can be modelled as the distribution from a single emitter at height \( h = H \) which is given in equation 5.6. Figure 5-8(b) depicts the radial probability distribution for the cases of uniform and surface absorption.

\[
PDF_{\text{uniform}}(r) = \frac{1}{H} \left( 1 - \frac{r}{H} \sqrt{4 + \left( \frac{r}{H} \right)^2} \right) \tag{5.5}
\]

\[
PDF_{\text{surface}}(r) = \frac{1}{H} \frac{r}{\left[ 1 + \left( \frac{r}{H} \right)^2 \right]^{3/2}} \tag{5.6}
\]

The resolution for a given LDC height and absorption profile can be characterized by \( R_P \), the radius within which \( P \) percent of the photons fall. \( R_P \) can be derived analytically for the case of uniform and surface absorption. As \( P \to 1 \), \( R_P \) can be simply expressed by equation 5.7 (see experimental). For the case of \( R_\sigma \), where \( \sigma = 68\% \) and \( R_{2\sigma} \), where \( 2\sigma = 95\% \), the resolution is \( R_\sigma \approx 3H \) and \( R_{2\sigma} \approx 20H \). Therefore LDC layers less than 1 \( \mu \)m thickness are expected to lead to minimal loss of image resolution for pixels greater than 20 \( \mu \)m in diameter.

\[
R_P \approx \frac{H}{1 - P} \tag{5.7}
\]

5.6 Experimental

5.6.1 QD Synthesis

PbS/CdS core/shell nanocrystals were synthesized using a large scale method based on previous procedures[97, 98]. To prepare PbS cores, 30 mmol of lead acetate trihydrate (Sigma Aldrich), 125 ml of octadecene (Sigma Aldrich) and 175 ml of oleic acid (TCI) are placed under vacuum for 12 hours at 100 C in a round bottom flask. This solution is placed under nitrogen and heated to 150 C. The sulfur precursors
Figure 5-8: (a) Cartoon of optical crosstalk due to the LDC layer. (b) Calculated radial probability distributions for uniform (blue line) and surface (red line) excitation distributions. Calculation done for a 1 μm thick LDC layer.

(150 ml of octadecene containing 15 mmol hexamethyldisilithiane (Fluka)) is rapidly injected using a pneumatic gun under vigorous mechanical stirring. After cooling to room temperature, this solution is transferred into a nitrogen glove box without air exposure. The QDs are purified by adding butanol and methanol until the solution is turbid, followed by centrifugation to precipitate the QDs. The supernatant is discarded and the QDs are redissolved in hexane.

PbS/CdS core/shell QDs are prepared using cation exchange[98]. Exchange is performed at 100 C for 6-24 hours under nitrogen using an excess of cadmium oleate. InAs/CdZnSe core/shell QDs were synthesized according to previously published procedure[99].

### 5.6.2 LDC Layer Characterization.

A 6% PMMA solution in chlorobenzene was prepared by sonication of 15,000 MW PMMA (Sigma Aldrich) chlorobenzene followed by filtration through a 0.45 μm filter. Films were either drop cast or spun coat 1500 rpm for 60 seconds. Film thickness were measured using a KLA Tencor P16 Surface Profilometer.
5.6.3 QD Volume Fraction Calculation

Leatherdale et. al. provide a method for determining the QD concentration from the absorption spectrum, the path length, the QD diameter and the bulk value for the complex refractive index[84]. This method is based on the theory that far above the band edge of the nanocrystal, the absorption will be the same per unit cell as in the bulk material. We use the complex refractive index of bulk PbS at 400 nm where n=3.7 and k=3.1[100].

InGaAs photodiodes were used as purchased from Hamamatsu Corporation, part number G8941-01. Electrical contact was made to the anode and cathode via silver paint and the samples were mounted on a glass substrate.

5.6.4 Refractive Index

Table 5.1 summarizes the effect of the QD volume fraction on the index of refraction and the calculated collection efficiency.

| Sample | PMMA Index | QD Film 2.9 | 3% QDs 1.49 | 10% QDs 1.5 |

Table 5.1: Index of refraction of polymer, QD blend as a function of QD concentration by volume. Index taken at 633 nm.

5.6.5 Optical Measurements

Absorption measurements were performed with a Carey 5000 UV-Vis-NIR spectrometer. For solution phase measurements trichlorotrifluoroethane was used as an infrared transparent solvent. Films were deposited on UV grade fused silica slides (Chemglass CGQ-0600-01). Emission spectra were taken using a Princeton Instruments Spectra Pro 300i spectrometer coupled to a Princeton Instruments OMA V InGaAs CCD array detector. The excitation source was a 632 HeNe laser, and the scattered excitation light was blocked with an 850 nm long pass filter.

External quantum efficiency measurements were taken using a Spectra Pro SP2150 equipped with a Xenon arc lamp to generate monochromatic light from 250 nm to 2000 nm.
nm. The intensity of light in the visible was measured with a calibrated Newport 818-UV enhanced Si photodiode and the infrared light was measured with a Newport 818-IR Ge photodetector. For each spectral region, appropriate long pass and short pass filters were used to isolate the monochromatic light. Short pass filters are particularly important for accurate measurements in the UV portion of the spectrum. Aluminium mirrors were used instead of lenses to prevent chromatic aberration over the broad spectral range used.

Transient photoluminescence measurements are taken using pulsed laser excitation from a 1064 nm diode laser and a high sensitivity, superconductive nanowire sensor.[101, 102].

5.6.6 Quantum Yield Measurements

The absence of a high QY dye with emission in the SWIR region prevents accurate relative QY measurements of the SWIR emitting QDs. For instance, the quantum yield of carbon nanotubes in solution is currently debated[103] due to uncertainty in the QY of IR-125 (Styrl-13), a common IR reference dye. The use of an integrating spheres provides a method for absolute QY measurements and allows for QY measurements of films. Absolute quantum yield measurements were performed with a barium sulfate coated integrating sphere system. For solution measurements, NMR tubes containing the fluorophore were inserted through a teflon block into the integrating sphere and the reference was a NMR tube with the an equal amount of the same solvent. For solid phase measurements, the QD/polymer film is deposited on a glass substrate which is held by a notched teflon block and a bare glass substrate is used as a reference. The excitation source is mechanically chopped at 80 Hz and the emission detected with a calibrated photodetector using a lock in amplifier (Stanford Research 830). For infrared QY measurements, a 780 nm CW diode laser was used for excitation and the scattered laser light and fluorescence were measured with a germanium detector (Newport 818-IR). A 850 nm long pass filter was used to selectively block the laser excitation so as to distinguish between scatter laser light and fluorescence. In the visible region, excitation was the 488 nm output of a multi line argon ion laser,
a 504 nm long pass filter is used to block the excitation light, and the scattered light and fluorescence are detected with a calibrated silicon detector (Newport 818-UV).

The quantum yield is determined according to supplemental equation 5.8, where $\eta_F$ is the external quantum efficiency (EQE) of the detector at the peak of the emission spectrum and $\eta_L$ is the EQE of the detector at the peak of the excitation laser frequency. $L$ is the current measured with the reference and no filter, $T$ is the current measured with the sample and no filter, and $F$ is the current measured with the sample and a filter to block the excitation light. We emphasize that not including the factor $\eta_L/\eta_F$, which for our experiments is approximately 2-3 due to the poor response of the Ge detector at 780 nm, leads to a tremendous error in the QY.

$$QY = \frac{F}{L - (T - F) \frac{\eta_L}{\eta_F}}$$  \hspace{1cm} (5.8)

In the visible region, the accuracy of the integrating sphere setup described above was tested against reference dyes with known quantum yield. For Rhodamine 101 (reference QY of 1.00, Exciton Dye Source), the quantum yield obtained was 0.99, and for Rhodamine B (reference QY of 0.31, Exciton Dye Source) the quantum yield was measured as 0.31.

5.6.7 Detector Band Transparency, $T_A(\lambda_{DC})$

The detector band transparency, $T_A(\lambda_{DC})$, is defined as the transparency of the LDC layer across the detector band ($\lambda_B$) for a given an average absorption of $A$ across the down conversion band, $\lambda_{DC}$. It can be calculated from the solution phase absorption spectrum using equation 5.9

$$T_A(\lambda_{DC}) = \frac{1}{\Delta \lambda_B} \int_{\lambda_B}^{\lambda_B} 10^{-\alpha(\lambda) X_A} d\lambda$$  \hspace{1cm} (5.9)

The absorbance spectrum is denoted $\alpha(\lambda)$ and $X_A$ is related to the number of fluorophores in the LDC layer required to reach an absorption of $A$. $X_A$ can be calculated with equation 5.10.
\[ 1 - A = \frac{1}{\Delta \lambda_{DC}} \int_{\lambda_{DC}}^{\infty} 10^{-\alpha(\lambda)X_A} d\lambda \]  

(5.10)

If \( \lambda_{DC} \) is approximated as a single wavelength, then \( X_A \) is given directly by equation 5.11.

\[ X_A = \frac{-\log (1 - A)}{\alpha(\lambda_{DC})} \]  

(5.11)

In this work we define \( \lambda_B \) as the wavelength region where the detector EQE is greater than 80% of its maximum. Since the detector EQE falls off quickly for InGaAs detectors, changing the threshold will not significantly effect \( T_A(\lambda_{DC}) \). In equation 5.10, the down conversion band, \( \lambda_{DC} \), is determined by the application of interest. In this work we set \( \lambda_{DC} = 300 \rightarrow 400 \) nm.

### 5.6.8 Approximations used in modelling collection efficiency and cross talk

In this chapter, a number of assumptions were made when calculating the collection efficiency and the amount of crosstalk, including isotropic emission, complete reflection at the LDC/air interface, and no reabsorption in the film. In general, accurately modelling the collection efficiency and crosstalk in the LDC layer is a complex calculation. In particular, the condition for isotropic emission in a medium is only satisfied when the emitter is farther from the edge of the medium than the wavelength of light in the medium. For a LDC layer on the order of 1 \( \mu \)m thick with QDs emitting light between 1-2 \( \mu \)m this condition will not be met, particularly near the air/LDC and LDC/detector interfaces. Emission near the interface between two, non absorbing, dielectric materials is considered in detail elsewhere[104, 105, 106], and is beyond the scope of this work. Qualitatively, the emitter will preferentially emit towards the high index medium. This will increase the CE, since the detector index is higher than the LDC layer index, and the LDC layer index is higher than that of air.
5.6.9 Cross Talk

The general expression for the probability distribution is given in equation 5.12, where the light emitted in the direction of the detector and the light emitted in the direction of the air-LDC interface are treated separately and give rise to the radial probability distributions $PDF_D (r; h, H)$ and $PDF_R (r; h, H)$ respectively. The light emitted away from the detector can be weighted by a reflection factor, $R (r; h, H)$, to account for the light that is transmitted through the LDC layer/air interface.

\[
PDF (r; h, H) = PDF_D (r; h, H) + PDF_R (r; h, H) R (r; h, H)
\]  

(5.12)

$R (r; h, H)$ is set to 1 when calculating the radial probability distribution functions for the case of uniform and surface absorption assuming complete reflection at the interface. $R (r; h, H)$ may be approximated using the Fresnel equations. Figure 5-9 shows the radial probability distributions for the cases of uniform and surface absorption in the LDC layer, factoring in reflection according to the Fresnel equations. The data is plotted normalized to the height of the LDC layer.

![Figure 5-9: Radial probability distribution function (PDF) calculated for the case of uniform absorption (a) and surface absorption (b) in the LDC layer. The solid black line corresponds to complete reflection at the LDC layer/air interface, while the solid red line factors in Fresnel type reflection at the interface. Dashed black and red lines represent, respectively, the PDF for light emitted towards the detector and light emitted away from the detector weighted by Fresnel reflection.](image)

The resolution is characterized by the radius, $R_P$, in which a given percentage $P$ of the photons fall. $R_P$ is calculated from equation 5.13.
\[ P = \int_0^{R_P} PDF(r) \, dr \quad (5.13) \]

For the cases of uniform and surface absorption in the LDC layer without reflection losses, \( R_P \) can be calculated with equation \( 5.13 \) using basic calculus and algebra and is given by equations \( 5.14 \) and \( 5.15 \) respectively.

**Uniform:**
\[ R_P = H \frac{P(2 - P)}{1 - P} \quad (5.14) \]

**Surface:**
\[ R_P = H \frac{\sqrt{P(2 - P)}}{(1 - P)} \quad (5.15) \]

In the limit \( P \to 1 \), both of these equations reduce to equation \( 5.16 \).

\[ R_P \approx \frac{H}{1 - P} \quad (5.16) \]

Table 5.2 gives the values for \( R_\sigma \) and \( R_{2\sigma} \) as calculated by equations \( 5.14-5.16 \), and numerically when Fresnel reflection included. The approximation in equation \( 5.16 \) closely agrees with the values derived for complete reflection. Since the reflection coefficient is higher for glancing angles at the LDC layer/air interface, factoring in reflection losses increases \( R_P \) by approximately 15%.

**Table 5.2:** \( R_\sigma \) and \( R_{2\sigma} \) for different models

<table>
<thead>
<tr>
<th>Method</th>
<th>( R_\sigma / H )</th>
<th>( R_{2\sigma} / H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H/(1 - P) )</td>
<td>3.13</td>
<td>20.0</td>
</tr>
<tr>
<td>Uniform</td>
<td>2.76</td>
<td>20.0</td>
</tr>
<tr>
<td>Surface</td>
<td>2.94</td>
<td>19.9</td>
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<tr>
<td>Uniform Fresnel</td>
<td>3.34</td>
<td>23.1</td>
</tr>
<tr>
<td>Surface Fresnel</td>
<td>3.46</td>
<td>23.1</td>
</tr>
</tbody>
</table>

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Appendix A

Contacts

A.1 Contact Types

There exists a great deal of literature on the nature of metal to semiconductor contacts. A quantitative analysis of ohmic and Schottky contacts can be found in *Photoelectronic Properties of Semiconductors* [62]. The specifics are of tremendous importance for thin devices such as photovoltaics where the accumulation or depletion region can extend a significant portion of the device length. The following discussion focuses on the terminology used in the photoconductor literature and the effects of the contacts on the current flow through the bulk of the semiconductor.

Traditionally, literature on photoconductors focused on lateral devices with channel lengths much greater than the depletion width of a Schottky depletion region. The contacts are characterized functionally as blocking, ohmic, and neutral for each charge carrier. A contact may, for example, be blocking for electrons and ohmic for holes. These contact types are depicted in figure A-1. For blocking contacts, the barrier to charge injection is large enough that there is negligible thermionic emission over the barrier into the film. For neutral contacts, sufficient thermionic emission exists such that at low current, the contact will appear ohmic in that it will supply sufficient electron density to meet the current being drawn through the film. However, once the current reaches a high enough level to deplete the carriers generated by thermionic emission, the contact will act as a blocking contact. Ohmic contacts
are those for which an accumulation region is present at the interface of the film and the metal. This accumulation region has greater charge density than the rest of the film. The accumulation region acts as a reservoir of charge for current flow and under high voltages will give rise to space charge limited current flow (see appendix B).

![Figure A-1: Cartoon depiction of different contact types.](image)

### A.2 Effect of Contact Types on the Dark Current

Consider the case of a p type semiconductor. When an electric field is applied between the contacts, mobile charges will flow towards the electrodes. For the case of ohmic contacts for hole injection, when a hole is collected at one contact, another hole is injected into the film to maintain charge neutrality. The hole current is dependent on the carrier density and mobility of the semiconductor, and all ohmic contacts will give the same current. If the contact is blocking for holes, holes can be extracted more quickly than they can be replenished. Some amount of space charge is likely to build up in the film, and the current will be limited by the low rate of thermionic emission over the Schottky barrier. The same is true for neutral contacts, with the exception that at low voltages, the rate of thermionic emission will be greater than the rate of holes being extracted at the electrodes and the current will appear ohmic.
A.3 Effect of Contact Types on the Photocurrent

If the contacts are blocking for electron and hole injection, then the maximum amount of photocurrent will be equal to the \( F \), the generation rate of photons in the material. In other words, the maximum photoconductive gain \( G \) will be unity. Once the electron or hole reach the contacts, they recombine in the external circuitry. Gains lower than unity will occur if there is any recombination in the semiconductor. This occurs if the lifetime of the carriers, \( \tau \), is shorter than the transit time, \( T_{tr} \). The gain can be expressed as the ratio of these two values (equation A.1)

\[
G = \frac{\tau}{T_{tr}} \tag{A.1}
\]

If the hole reaches the contact before the electron, some amount of space charge will build up in the material. If the electron is deeply trapped and can not be extracted, charge will build up in the film until it cancels out the electric field and no current will flow.

If the contacts are ohmic for hole injection (again considering the case of a p type semiconductor), when the hole reaches the electrode (the cathode(-)), another hole will be injected from the opposing electrode (the anode(+) ) to maintain charge neutrality in the film. The hole will cycle through between the electrodes until it recombines with the electron, resulting in photoconductive gain. As above, the gain is simply the lifetime divided by the transit time. The difference is that now the lifetime of the hole can be larger than the transit time, since it is replenished by the ohmic contact. The result is the expression for the gain given by equation A.2.

\[
G = \frac{\mu \tau V}{L^2} \tag{A.2}
\]

Similar to the case of ohmic dark current, there is no effect of the electrodes on the recombination of the electron and hole. However the current may still depend on the contacts at higher voltages if the cathode(-) is blocking for electrons. Consider the case of low mobility electrons. At low voltages, the lifetime of the electron will
be shorter than the transit time, and recombination will occur in the semiconductor before the electron reaches the anode (+). At higher voltages, the electron will reach the anode (+). If the cathode (-) is injecting for electrons, then an electron from the cathode (-) will be injected into the semiconductor when the electron reaches the anode (+). The recombination will continue to occur in the semiconductor and equation A.1 will be unaffected. If the cathode (-) is blocking for electron injection, then recombination between the electron and hole will occur in the external circuit, as every time an electron is extracted, a hole will no longer be injected from the anode (+) to maintain charge neutrality. The result is that the current will saturate. This is because the lifetime of the hole becomes equal to the electron transit time ($\tau_h = T_{tr,e}$. $T_{tr,e}$) decreases with electric field at the same time as the velocity of the hole increases with electric field (equation A.3).

$$G = \frac{\mu_h T_{tr,e} V}{L^2} = \frac{\mu_h V L^2}{\mu_e V L^2} = \frac{T_{tr,e}}{T_{tr,h}} = \frac{\mu_h}{\mu_e}$$ \hspace{1cm} (A.3)

We have not included the contribution of the electron to the gain in equation A.3. Since the electrode is mobile, it will contribute to the gain, and the correct expression for the gain at saturation is A.4.

$$G = \frac{\mu_h + \mu_e}{\mu_e}$$ \hspace{1cm} (A.4)

Equation A.3 and equation A.4 are approximately equal if $\mu_h$ is much larger than $\mu_e$. 

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Appendix B

Space Charge Limited Current Flow

B.1 Introduction

The following is a discussion of space charge limited current (SCLC). It relies on the treatments by Rose[71] and Bube[62]. This is an important phenomena in some semiconductor systems, and insignificant in others. Whether SCLC flow occurs depends on the contact and the film properties, particularly the carrier density, as will be discussed below.

B.2 A Comment on Ohmic Contacts

A key concept that is not always thoroughly discussed is the nature of the ohmic 'reservoir' of electrons. A standard image of space charge limited current flow is shown in figure B-1(a). The electrons in the reservoir are in the conduction band of the semiconductor, and a positive voltage is applied to the opposing contact. Naively, it would appear that the electrons would all flow out of the reservoir and into the film towards the opposing positive charge. What is implicitly draw into this picture is that there exists a large amount of positive charge on the electrode contacting the reservoir which holds most of the electrons in place. The electrons in the reservoir
were injected from the metal when the Fermi levels equalized, in the opposite manner of a Schottky junction (figure B-1(b)). For every negative charge in the reservoir, there is a positive charge on the metal. This creates the potential well depicted in figure B-1(a). When a voltage is applied between the two plates, the contact takes on a charge $Q = CV$ in accordance with the capacitance between the electrodes. For the ohmic contact at the cathode, the effect of adding negative charge to the contact is to reduce the positive charge that is holding the electrons in the accumulation reservoir, as depicted in figure B-1(c). These carriers may now enter the film and flow toward the anode. This is why only an amount of charge equal to $Q = CV$ enters the film.

![Figure B-1: Cartoon of mechanism for space charge limited conduction](image)

Figure B-1: (a) Cartoon of mechanism for space charge limited conduction (b) Depiction of the charge distribution in the contact (red triangle) and in the semiconductor electron reservoir (blue triangle). (c) Application of a bias to the contact frees an equal amount of charge from the reservoir.
B.3 Vacuum Tubes

When a metal is heated to a high enough temperature, electrons will gain sufficient thermal energy to undergo thermal emission over the barrier into the vacuum. This is the process used in vacuum electronics to create conduction between parallel plates, and the first system in which space charge limited current (SCLC) was observed. As discussed above, when the electrons boil off the metal, they leave behind a positive charge and a potential well is created since the electrons attracted to the metal. The cathode contact supplies the electrons, which will be drawn towards the other side of the vacuum tube. Therefore it is the cathode. When a positive charge is applied to the other side (the anode), the capacitance of the system will induce an amount of negative charge on the cathode per unit area, $Q$, as given by equation B.1 where $\epsilon$ is the dielectric constant of the material, $\epsilon_o$ is the static dielectric constant, $V$ is the voltage and $L$ is the distance between the metal plates.

$$Q = CV = \frac{\epsilon \epsilon_o V}{L} \tag{B.1}$$

This amount of electrons will be freed from the cathode and will travel across the vacuum tube to the anode. The amount of current will be equal the amount of charge between the electrodes divided by transit time $T_{tr}$ as expressed in equation B.2, where $\overline{v}$ is the average electron speed.

$$I = \frac{Q}{T_{tr}} = \frac{\overline{v} \epsilon \epsilon_o V}{L^2} \tag{B.2}$$

It can be shown that the average velocity of the electrons is given by equation B.3 where $m$ is the mass of the electron.

$$\overline{v} = \frac{1}{2} \left( \frac{qV}{m} \right)^{1/2} \tag{B.3}$$

Combining equations B.2 and B.3 gives an equation for the space charge limited current in a vacuum tube.
\[ I_{\text{vacuum}} = \frac{1}{2} \left( 2 \frac{qV}{m} \right)^{1/2} \] (B.4)

## B.4 SCLC in Semiconductors and Insulators

SCLC is also observed in insulators and semiconductors with ohmic contacts. Due to scattering and trapping, the velocity of the electron is significantly less than in the vacuum tube case and is determined by the electric field and mobility. The presence of free carriers and traps within the material also give rise to more complex results than in the case of the vacuum. Rewriting equation B.2 for the case of a semiconductor gives equation B.5, where \( \mu \) is the mobility, and \( E \) is the electric field.

\[ I = \frac{Q}{T_{\text{tr}}} = \frac{\mu \epsilon \epsilon_0 V}{L^2} \] (B.5)

Expressing in terms of voltage gives the incorrect expression for the SCLC in the semiconductor in equation B.6.

\[ I = \frac{Q}{T_{\text{tr}}} = \frac{\mu \epsilon \epsilon_0 V^2}{L^3} \] (B.6)

The reason this equation is slightly incorrect is that the amount of charge being injected into the semiconductor was assumed to be given by equation B.1. However, the charge no longer rests on the cathode, but is spread throughout the semiconductor as illustrated in figure B-1(a). This has the effect of increasing the capacitance, and therefore the amount of charge injected, just as having a shorter gap between the electrodes would give rise to a larger capacitance. The electrode is effectively distributed throughout the film. The effect is small however, since most of the charge is still near the cathode as depicted in figure B-1(a), and leads to the addition of the \( 9/8 \) constant in front of the correct SCLC current equation.

\[ I = \frac{9 \epsilon \epsilon_0 \mu V^2}{8 L^3} \] (B.7)

The author finds that often SCLC is used as an explanation superlinear IV curves
in a way that is not convincing. As is noted below, often the power is not 2 due to 
traps, and so the data is fitted with $V^p$. One can imagine that over a small range of 
voltages, many superlinear curves can be fit to the equation $I = aV + bV^p$ which may 
have nothing to do with space charge limited currents (Consider the Taylor expansion 
of $\exp(V/V_o)$ for instance). The $L^{-3}$ dependence is much more striking and rare, and 
suggests that varying the electrode size is a good way to prove the presence of SCLC.

B.5 Transition from Ohmic to SCLC Currents

Below an onset voltage, $V_{onset}$, the SCLC current will be below the ohmic current. 
After $V_{onset}$, the quadratic dependence of the SCLC current on voltage will result 
in the SCLC dominating the conduction. Often $V_{onset}$ is derived by looking at the 
dielectric relaxation time, $\tau$, of the material. The dielectric relaxation time will be 
discussed below. A simpler concept which leads to the same result is to define $V_{onset}$ 
as the point at which the SCLC current equals the ohmic current as expressed in 
equation B.8 where $n$ is the carrier density.

$$\frac{q\mu V_{onset}}{L} = \frac{9 \epsilon \epsilon_0 \mu V_{onset}^2}{8 L^3}$$  \hspace{1cm} (B.8)

Solving gives equation B.9.

$$V_{onset} = \frac{qnL^2}{\epsilon \epsilon_0}$$  \hspace{1cm} (B.9)

Before discussing the dielectric relaxation time, a few things are worth noting. The 
higher the carrier density, the higher the onset for SCLC. Carrier density is a number 
that can vary by many orders of magnitude between samples. An increase in the 
dielectric constant increases the capacitance of the system and therefore the space 
charge. Finally, closely space electrodes will have a significantly lower SCLC current 
threshold.
B.6 Dielectric Relaxation Time

The onset voltage is usually derived in terms of the dielectric relaxation time. The dielectric relaxation time is equal to the dielectric constant over the conductivity (equation B.10).

\[ \tau = \frac{\varepsilon \varepsilon_0}{\sigma} = \frac{\varepsilon \varepsilon_0}{q n \mu} \]  \hspace{1cm} (B.10)

It can be understood as the time to respond to a change in the charging in the film. In other words, it is the time required to compensate a charge imbalance in the film. The higher the conductivity, the faster charges can move within the film to balance out the charge and the lower the dielectric relaxation time. The higher the dielectric constant, the more the charge is screened by dipole rearrangement in the film. This results in a lower force on the free carriers to rearrange and increases the dielectric relaxation time. For example, consider a semiconductor between ohmic electrodes that is suddenly bombarded in the middle with a pulse of negatively charged electrons. This creates a charge imbalance in the film which is an unstable condition. The dielectric relaxation time gives a measure of how quickly new holes will enter the sample and/or electrons will leave the sample to restore charge neutrality.

In the case of SCLC, the electrode is injecting carriers into the film. If the transit time of the carriers \((T_{tr})\) is large compared to the dielectric relaxation time \(\tau\), the charges in the film will rearrange to prevent the added charge from building up and creating a charge imbalance between the electrodes. When the transit time of the carriers becomes faster than the dielectric relaxation time, the space in between the electrodes begins to develop a charge (hence space charge). It is no longer electrically neutral. The electric field is no longer constant between the two electrodes, but instead drops predominately across the portion of the film that does not have any space charge (see figure B-1(a)). The onset voltage can be expressed as the voltage at which the transit time matches the dielectric relaxation time as shown in equation B.11.
\[
\frac{\mu V}{L^2} = \frac{\epsilon \varepsilon_o}{q n \mu} \quad \text{(B.11)}
\]

The result for \( V_{\text{onset}} \) is the same as for equation B.8 and is given by equation B.9.

### B.7 The Effect of Traps

The previous discussion was for the case of no traps. If a large number of traps \( n_t \) exist, then not all of the charge entering the film will result in additional carriers moving through the film. Instead the charge will settle to the Fermi level \( (E_f) \). This is similar to the case of the field effect transistor measurement, where the back gate induces charge in the film which also settles over time to the Fermi level. In the case of shallow traps, where the Fermi level is within \( kT \) of the conduction band, the effect will be that the number of mobile charge carriers added will be \((n/n_t)Q\). The onset voltage with shallow traps, \( V_{\text{onset, shallow}} \), is related to the trap free case as given by equation B.12

\[
V_{\text{onset, shallow}} = \frac{n_t}{n} V_{\text{onset}} \quad \text{(B.12)}
\]

The case of deep traps is significantly more complicated. The assumption for shallow traps was that since the traps are within \( kT \) of the conduction band, the probability of being in a trap or the conduction band is only related to the density of states. For deep traps where the Fermi level lies greater than \( kT \) from the conduction band the percentage of carriers entering the conduction band will be exponentially smaller than the carriers entering into the trap states. The first effect is that the onset voltage is significantly increased. The addition of charge will begin to change the Fermi level however, just as photoexcitation changes the Fermi level. The result is the a quasi Fermi level will develop, \( E_{fn} \). Since the quasi Fermi level is closer to the conduction band than the Fermi level, the carrier concentration will increase and space charge currents will eventually be observed, although at a higher voltage than for the trap free or shallow trap case. Also, the slope of the SCLC current-voltage
curve will no longer be quadratic, but will instead depend on the nature of the trap
distribution as discussed in detail by Rose[71].
Appendix C

Meyer Neldel Rule and the Statistical Shift of the Fermi Level

A concept with is frequently discussed in literature is that of the Meyer-Neldel relation. This is an empirical relation observed by Meyer-Neldel that has been found to be true for a great number of systems and which states that for a given system, the prefactor \( \sigma_0 \) in equation C.1 is related to the activation energy, \( E_{\text{sigma}} \), as described by equation C.2.

\[
\sigma(T) = \sigma_0 \exp(-E_\sigma/kT) = \sigma_0 \exp(-(E_c - E_F/kT)) \tag{C.1}
\]

\[
\ln(\sigma_0) = \ln(\sigma_{oo}) + E_\sigma/kT_m \tag{C.2}
\]

In equation C.2 \( \sigma_{oo} \) is a the characteristic conductivity of the material. For example, a material might have different levels of dopant atoms added. In each case, \( \sigma_{oo} \) is the same, but \( \sigma_0 \) varies according to equation C.2. A characteristic temperature, \( T_m \), can be defined such that the conductivity will be the same for each sample at this temperature. \( T_m \) is also a property of the material. The current can be described in terms of \( T_m \) and \( \sigma_{oo} \) by equation C.3. This is shown in figure C-1.

\[
\sigma(T) = \sigma_{oo} \exp(E_\sigma/kT_m - E_\sigma/kT) \tag{C.3}
\]
Figure C-1: Theoretical current-temperature curves calculated using the Meyer Neldel Rule (equation C.3) for different $E_\sigma$ values. The curves converge at $T_m$.

There is no definitive explanation of the universality of the observed behaviour. The Meyer-Neldel rule can be expressed as equation C.4, where $\gamma$ is a first order correction term.

$$E_c - E_F = (E_c - E_F)_0 - \gamma T$$  \hspace{1cm} (C.4)

This suggests that there is a temperature dependent shift in the activation energy. This could be due to a shift in the band gap of the material with temperature or a shift in the Fermi level. The latter condition is frequently referred to as the 'statistical shift of the Fermi level' and occurs when the Fermi level moves away from the conductive state with increasing temperature. This will occur if the Fermi level lies within an asymmetrical density of states such as an exponential band tail. This can be understood by considering the effects of increasing temperature from the $t=0$ condition. At $t=0$, all states below $E_F$ are occupied with electrons. As the temperature
increases electrons are excited above the t=0 Fermi level. The number of electrons above the Fermi level is given by the Fermi distribution multiplied by the density of states. The number of vacancies below the Fermi level is similarly calculated. The number of electrons must equal the number of vacancies and this will only be true if the Fermi level shifts to a lower value.
Appendix D

Stokes Shift and Franck Condon Principle

D.1 Franck-Condon Principle

Figure D-1(a) shows the absorption and emission spectra of Rhodamine 590. Two striking features of the two spectra are the shift between the emission and the absorption, as well as the mirror symmetry between the absorption and emission. These effects are due to vibrational relaxation and are explained by the Franck-Condon principle as depicted in figure D-1(b). The Franck-Condon principle states that the transition between the electronic ground state $S$ and the excited state $S^*$ occurs faster than the nuclei can rearrange. Therefore there must be overlap between the nuclear configuration of the initial and the excited state. The vibrational ground state of the excited electronic state, $S_0^*$, will be different than the initial vibrational ground state, $S_0$, and there may be poor overlap between these two states. A stronger transition is often observed between $S_0$ and $S_1^*$ as depicted by the left blue arrow. When the exciton is created, it will relax to its lowest vibrational configuration. Due to symmetry in the overlap between states $S_0 \to S_1^*$ and $S_0^* \to S_1$, the chance of decaying via $S_0^* \to S_1$ relative to other pathways is similar to chance of excitation through $S_0 \to S_1^*$. This results in the symmetry in the peak amplitudes. Transitions to higher lying vibrational states require a higher excitation energy, and give off correspondingly
Figure D-1: (a) Absorption and emission spectra of Rhodamine 590 dye displaying near mirror symmetry in the absorption and emission profiles. (b) Franck-Condon diagram. Excitation from the ground state to a high lying vibrational state is mirrored by emission from the ground vibration state of the electronically excited state to a vibrationally excited state of the ground electronic state (blue and green arrows).
Appendix E

Down Conversion Derivations

E.1 Introduction

The equations used in the down conversion chapter are derived here for reference. No complicated math is involved beyond basic calculus and arithmetic.

E.2 Surface Distribution

The probability distribution of the emission profile of an emitter on the surface at height $H$ can be shown to be given by equation E.1.

$$PDF_{\text{surface}}(r) = \frac{1}{H} \frac{\frac{r}{H}}{\left[1 + \left(\frac{r}{H}\right)^2\right]^{3/2}} \quad (E.1)$$

The percentage of photons striking the detector within a distance $X_P$ of the emitter is given by equation E.2

$$P = \int_0^{X_P} \frac{Hr}{(H^2 + r^2)^{3/2}} \, dr \quad (E.2)$$

This can be simplified as follows:

$$P = \frac{H}{\sqrt{H^2 + r^2}} \bigg|_0^{X_P}$$
\[
P = 1 - \frac{H}{\sqrt{H^2 + X_P^2}}
\]

\[
(1 - P) = \frac{H}{\sqrt{H^2 + X_P^2}}
\]

\[
\sqrt{H^2 + X_P^2} = \frac{H}{(1 - P)}
\]

\[
H^2 + X_P^2 = \frac{H^2}{(1 - P)^2}
\]

\[
X_P = \sqrt{\frac{H^2}{(1 - P)^2} - H^2}
\]

\[
X_P = H \sqrt{\frac{1}{(1 - P)^2} - 1}
\]

\[
X_P = H \sqrt{\frac{P(2 - P)}{(1 - P)^2}}
\]

\[
X_P = H \frac{\sqrt{P(2 - P)}}{(1 - P)} \quad (E.3)
\]

### E.3 Uniform Distribution

The probability distribution of the emission profile of an emitter distributed uniformly through a film of height \(H\) can be shown to be given by equation E.4.

\[
PDF_{\text{uniform}}(r) = \frac{1}{H} \left(1 - \frac{r}{H} \sqrt{4 + \left(\frac{r}{H}\right)^2}\right) \quad (E.4)
\]

The percentage of photons striking the detector within a distance \(X_P\) of the emitter is given by equation E.5. The equation accounts for both photons emitted towards and photons emitted away from the detector.
\[ P = \frac{1}{2} \left( \int_0^{X_P} \frac{1}{H} \frac{r}{H \sqrt{H^2 + r^2}} dr + \int_0^{X_P} \frac{r}{H \sqrt{H^2 + r^2}} - \frac{r}{H \sqrt{4H^2 + r^2}} dr \right) \quad (E.5) \]

This can be simplified as follows:

\[ P = \frac{1}{2} \left( \frac{r}{H} - \frac{\sqrt{H^2 + r^2}}{H} \bigg|_{0}^{X_P} + \frac{\sqrt{H^2 + r^2}}{H} - \frac{\sqrt{4H^2 + r^2}}{H} \bigg|_{0}^{X_P} \right) \]

\[ P = \frac{1}{2} \left( \frac{\sqrt{H^2 + X_P^2}}{H} - \frac{\sqrt{4H^2 + X_P^2}}{H} + 1 + \frac{X_P}{H} - \frac{\sqrt{H^2 + X_P^2}}{H} + 1 \right) \]

\[ (P - 1) = -\frac{\sqrt{4H^2 + X_P^2}}{2H} + \frac{X_P}{2H} \]

\[ 2H(1 - P) = \sqrt{4H^2 + X_P^2} - X_P \]

\[ (2H(1 - P) + X_P)^2 = 4H^2 + X_P^2 \]

\[ 4H^2(1 - P)^2 + X_P^2 + 4H^2(1 - P)^2 X_P = 4H^2 + X_P^2 \]

\[ H(1 - P)^2 + (1 - P)X_P = H \]

\[ H(1 - P)^2 + (1 - P)X_P = H\frac{1 - (1 - P)^2}{1 - P} \]

\[ X_P = H^2 \frac{P - P^2}{1 - P} \quad (E.6) \]
Approximation

Both the uniform case (equation E.6) and surface case (equation E.3) approach equation E.7 as $P \to 0$. This is the result used in the text.

$$X_P = H \frac{H}{1 - P}$$  \hspace{1cm} (E.7)
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