COLLOIDAL QUANTUM DOT
SCHOTTKY BARRIER PHOTODIODES

by

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Abstract

Herein, we report the first solution-processed broadband photodetectors to break the past compromise between sensitivity and speed of response. Specifically, we report photodiodes having normalized detectivity ($D^*$) $> 10^{12}$ Jones and a 3dB bandwidth of $> 2.9$ MHz. This finding represents a 170,000 fold improvement in response speed over the most sensitive colloidal quantum dot (CQD) photodetector reported$^1$ and a 100,000 fold improvement in sensitivity over the fastest CQD photodetector reported$^2$.

At the outset of this study, sensitive, solution-processed IR photodetectors were severely limited by low response speeds$^1$. Much faster response speeds had been demonstrated by solution-processed photodetectors operating in the visible$^3$, but these devices offered no benefits for extending the spectral sensitivity of silicon. No available solution-processed
photodetector combined high sensitivity, high operating speed, and response to illumination across the UV, visible and IR.

We developed a fast, sensitive, solution-processed photodetector based on a photodiode formed by a Schottky barrier to a CQD film. Previous attempts to form sensitive photodetectors based on CQD photodiodes had demonstrated low quantum efficiencies that limited sensitivity\(^4\,^5\).

Efficient, sensitive semiconductor photodiodes are based on two fundamental characteristics: a large built-in potential that separates photogenerated charge carriers and minimizes internal noise generation, and high semiconductor conductivity for efficient collection of photogenerated charge. Schottky barriers to CQD films were developed to provide high, uniform built-in potentials. A multi-step CQD ligand exchange procedure was developed to allow deposition of tightly packed films of CQDs with high mobility and sufficiently well-passivated surfaces to form high-quality metallurgical junctions.

The temporal response of the CQD photodiodes showed separate drift and diffusion components. Combined with detailed measurements of the Schottky barrier, these characteristics provided the physical basis for a numerical model of device operation. Based on this understanding, devices that excluded the slow diffusive component were fabricated, exploiting only the sub-microsecond field-driven transient to achieve MHz response bandwidth.
These devices are the first to combine megahertz-bandwidth, high sensitivity, and spectral-tunability in photodetectors based on semiconducting CQDs. Record performance is achieved through advances in materials and device architecture based on a detailed understanding the physical mechanisms underlying the operation of CQD photodiodes.
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I am also grateful to my colleagues in Professor Sargent’s research group. I have not encountered a greater richness of talent or diversity of skills in any other setting.

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List of Acronyms

BDT  benzene dithiol
CQD  colloidal quantum dot
DR   depletion region
IR   infrared
NC   nanocrystal
NIR  near infrared
OCVD open circuit voltage decay
PBA  primary butyl amine
PC   photoconductive
PL   photoluminescence
PV   photovoltaic
QNR  quasi-neutral region
RC   resistance capacitance
SRH  Shockley Read Hall
SSPG steady state photocarrier grating
SWIR short wavelength infrared
TOF  time-of-flight
UV   ultraviolet
XPS  X-ray photoelectron spectroscopy
Chapter 1. Introduction

1.1 Optical Radiation Detection

Light detection is an important sensory mechanism throughout biology and technology. Flora and fauna alike have adapted to take advantage of the abundance of light available in the ultraviolet (UV), visible, and infrared (IR) afforded by Earth’s proximity to the Sun. Human interest in light naturally centres on the visible part of the spectrum. Over the last several hundred years, our ability to detect and measure light has expanded to include UV and IR wavelengths through the development of detectors to supplement the range of sensitivity of the human eye. Detection of light currently forms the basis of a wide variety of technologies spanning optical communications, remote sensing, metrology, and image capture. High-sensitivity detection of light is fundamental to a huge commercial market – image sensors alone represent a 7 billion U.S. dollar portion of the 16 billion U.S. dollar semiconductor optoelectronics industry in 2007.

The fundamental performance characteristics of a photodetector are sensitivity and speed of operation. In many photodetectors, an architectural compromise is required between speed and sensitivity; however, ideally, a photodetector should be both very fast and very sensitive.
The spectral response of a detector is closely tied to its intended application. Typically the range of spectral response is intentionally limited to the wavelengths of the signal to be detected in order to reduce sensitivity to noise sources. Detection of light at IR wavelengths is particularly useful, allowing detection of light transmitted through atmospheric\textsuperscript{7}, biological\textsuperscript{8,9}, and other materials absorption windows. Specific applications that depend on IR light detection include:

- optical fibre communication networks
- night vision and night sky illumination for security and surveillance
- thermal imaging for search-and-rescue and industrial monitoring
- astronomy
- satellite monitoring of geology and weather
- eye-safe, free-space laser applications such as LIDAR
- spectrometry

### 1.2 Limitations of Existing Photodetectors

Optical detectors commonly make use of semiconductors to convert incident photons to electronic charge carriers which are subsequently collected and quantified. These devices are typically fabricated in a monocrystalline semiconductor substrate grown epitaxially or formed in a melt. The size of the detectors is limited by the high cost of the substrates and any additional deposition of lattice-matched semiconductor materials. Additionally, these substrates are, by their crystalline nature, rigid and brittle. These physical proprieties of traditional semiconductor materials limit the range of potential applications of the detectors, and the integration of optical detection systems.
When fabricating an optical detection system, it is desirable to integrate, as closely as possible, the optoelectronic detection devices and the electronic charge carrier processing devices. The motivations for integration are multifold, but typically include maximizing the density of detectors, their operating speed, and their overall sensitivity while reducing manufacturing costs associated with die-by-die hybrid integration, system size and weight, and power consumption.

Visible and UV light can be detected by silicon – ubiquitous in modern microelectronics – allowing fabrication of optical detectors and signal processing circuitry in a single substrate. However, the bandgap of silicon is too wide to provide sensitivity to the IR. IR detectors are commonly implemented using narrow bandgap semiconductors such as Ge, InSb, InGaAs, HgCdTe, and lead salts\textsuperscript{10}. Optical detectors fabricated using these materials have enjoyed many years of development and generally demonstrate excellent performance, however densely integrated signal processing electronics are not available in these materials.

Due to the lattice matching requirements of crystalline semiconductors, established IR sensitive materials are structurally incompatible with silicon. This constraint prevents monolithic integration of IR detectors with microelectronics signal processing circuitry. As a result, IR detection systems are typically composed of multiple semiconductor substrates connected with mechanical bonds to form a hybrid device. The degree of integration and the performance of these systems are thus severely curtailed: the operating speed, number of photodetectors, and their size and spacing are limited by the
size, yield, reliability, and cost of the bonds. To illustrate the severity of the limitations imposed by hybridization, we compare typical parameters of InGaAs-on-Si hybrid imaging arrays with visible-only silicon imaging arrays in Table 1.1.

Table 1.1. Parameters of hybrid and integrated silicon imaging arrays.

<table>
<thead>
<tr>
<th>Array Type</th>
<th>Spectral Range [nm]</th>
<th>Pixel Count</th>
<th>Pixel Size [μm]</th>
<th>Cost [USD]</th>
</tr>
</thead>
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<tr>
<td>InGaAs-on-Si</td>
<td>900 to 1700</td>
<td>&lt;100k to 300k</td>
<td>~30</td>
<td>1000 to &gt;10,000</td>
</tr>
<tr>
<td>Integrated Silicon</td>
<td>350 to 1100</td>
<td>1M to &gt;10M</td>
<td>~1</td>
<td>&lt;1 to 100</td>
</tr>
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1.3 New Materials for High Performance Photodetectors

1.3.1 Solution-Processed Semiconductors and Devices

Solution-processed semiconductors include organic materials such as polymers and small molecules, and organic-inorganic hybrids such as colloidal quantum dots. The defining features of solution-processed semiconductors are that their growth, or synthesis, as well as their subsequent processing to form devices, takes place while dispersed in a liquid medium. This is in contrast to growth on a solid substrate, as is required in the case of crystalline semiconductors. As a result, the structural and electronic properties of solution-processed semiconductors are independent of the substrate onto which they are ultimately deposited, eliminating the lattice matching requirements inherent in the growth of crystalline semiconductors. This structural independence allows deposition of solution-processed semiconductors onto an unmatched variety of substrates ranging from...
rigid glasses and crystalline materials to flexible metals and plastics. Additional benefits of solution-processing include low cost, large area deposition and physical flexibility.

The compatibility of solution-processed semiconductors with such a wide range of substrates – including crystalline semiconductors such as silicon – makes them an attractive medium for implementing integrated optoelectronics devices. Direct integration of solution-processed photodetectors with organic circuits\textsuperscript{11,12}, microfluidics\textsuperscript{13,14}, and optical circuitry\textsuperscript{11,15}, and commercial microelectronics have been demonstrated.

Photodetectors based on solution-processed semiconducting polymers have shown promise; however, despite recent advances, absorption in semiconducting polymers has been limited to wavelengths < 1000 nm\textsuperscript{16}. The bandgap and spectral range of these materials is fixed by their composition, offers no advantage over silicon, and precludes their use in many IR photodetector applications.

### 1.3.2 Colloidal Quantum Dots

Colloidal quantum dots (CQDs) are nanoscale semiconductor particles that combine quantum size effect tuning of their electrical and optical properties with the practical advantages of solution processing. Control over the bandgap, and the variety of materials available to form CQDs, provides optical absorption covering the ultraviolet, visible, and infrared (IR). CQD absorption onsets have been demonstrated at wavelengths up to 2000 nm for PbS CQDs\textsuperscript{8}, and 3000 nm for HgCdTe CQDs\textsuperscript{17}.
The bandgap energy separating the valence and conduction band edges of a semiconductor determines the spectral absorption cutoff. In bulk semiconductors, this energy is defined by the composition and organization of atoms in the crystal lattice. If the dimensions of the semiconductor are reduced to less than \( \sim 10 \text{ nm} \), the quantum size effect begins to influence the electronic properties of the material, and the bandgap becomes dependent on the size of the crystal.

In addition to providing absorption at longer wavelengths, the ability to tune the bandgap to limit spectral absorption is also important. As the absorption onset of a semiconductor is shifted to longer wavelengths by reducing the effective bandgap, the rate of internal thermal noise generation and sensitivity to background thermal radiation increases. For photodetector applications, the bandgap of a semiconductor should only be as small as necessary to absorb photons of interest, while rejecting longer-wavelength photons and minimizing internal noise that would otherwise limit sensitivity. A detailed examination of the dependence of photodetector sensitivity on absorption cutoff is presented in Section 4.2.

An overview of the structure, synthesis, and electronic and optical properties of CQDs shows how the fundamental properties of these materials are related and how they can be controlled.
1.3.2.1 Structure

Semiconductor CQDs consist of very small crystals of semiconductor material (~1 nm to ~10 nm in diameter) surrounded by a layer of organic ligands. The ligands are chemically bonded to the surface of the crystal, providing electronic and chemical passivation of dangling bonds and solubility in polar or non-polar solvents, determined by the ligand species. Surface passivation is critical for controlling electronic surface states that would otherwise overwhelm the electronic properties of the semiconductor core due to the very high surface-to-volume ratio.

Figure 1.1a shows a high resolution TEM image of a single PbS CQD surrounded by a layer of disordered organic material corresponding to the ligands. The diffraction pattern produced by the atoms in the highly-ordered crystalline core is clearly visible. CQDs of similar size form films with relatively uniform inter-dot spacing and short range ordering, as shown in Figure 1.1b.

Figure 1.1. High resolution TEM images of PbS CQDs. (a) A close-up view of a single CQD showing the diffraction pattern of the highly-ordered crystalline core. (b) A monolayer of close packed CQDs showing short range ordering. Reprinted with permission from 19. Copyright 2003 Wiley-VCH Verlag GmbH & Co. KGaA.
Colloidal quantum dots are a type of nanocrystal. Semiconductor nanocrystals are an intermediate size of structure between molecular semiconductors and bulk crystalline materials. There is no firm boundary between these domains, however a range of ~100 to ~10,000 atoms per particle corresponds to the nanocrystal form\textsuperscript{18}. The lower limit of the nanocrystal size range is limited by the stability of the bulk crystalline lattice while the upper limit represents sizes where carriers become mobile within the nanocrystal\textsuperscript{18}. The semiconducting nanocrystals considered in this work are approximately spherical, resulting in a similar degree of quantum confinement in all three spatial directions. Nanocrystals of this type are quantum dots. Synthesis and processing in a liquid dispersion provide further distinction and identify these materials colloidal quantum dots.

1.3.2.2 Synthesis

The most successful synthesis, in terms of the overall uniformity and quality of semiconductor CQDs, entails pyrolysis of metal-organic precursors in hot (120-360 °C) coordinating solvents\textsuperscript{18}. The organometallic CQD growth process is illustrated schematically in Figure 1.2. Typically, one precursor is mixed with the coordinating solvent and held at a steady temperature. The other precursor is then injected into this mixture (Figure 1.2, stage 1), resulting in spontaneous nucleation (Figure 1.2, stage 2). Nucleation results from the thermal decomposition of the precursor agents upon injection, and supersaturation of monomers that form the building blocks of the CQDs. Nucleation is followed by relatively rapid growth of the crystalline semiconductor cores of CQDs. Growth may be followed by slower Ostwald ripening (sacrificial dissolution of smaller, higher-surface-energy particles to enable the growth of larger particles) after one or more
of the precursors are exhausted (Figure 1.2, stage 3). The synthesis reaction may take anywhere between several seconds up to several hours to reach completion, depending on the materials involved.

![Figure 1.2](image)

Figure 1.2. A schematic representation of the organometallic CQD growth process. Synthesis results in inorganic crystalline semiconductor cores surrounded by organic ligands that passivate the crystal surface, as shown in the final step of the growth process. Reproduced with permission from\textsuperscript{20}. Copyright 2001 Bryan Christie Design.

The synthesis monomers shown in Figure 1.2, stage 1 include metallic atoms bound to one or more molecules of the coordinating solvent (balls with tails in the figure), and the second component of the compound semiconductor, which may or may not be bound to a coordinating solvent (balls without tails in the figure). When attached to a semiconductor atom, the coordinating solvent acts as a ligand, providing solubility and controlling the rate of monomer interaction and CQD growth. After nucleation, the CQD cores are surrounded by a ligand layer that provides solubility and prevents individual CQDs from aggregating during or after synthesis.
1.3.2.3 Electronic Properties

CQDs offer wide-ranging, yet finely-tuned, selection of semiconductor bandgap through the quantum size effect. Quantum confinement within individual CQDs is determined by nanoscale dot diameter and is controlled during self-assembly.

Quantum Size Effect

Quantum-size effects become apparent when dimensions of a structure are comparable to the natural length scale of electrons and holes, resulting in a dependence of particle behaviour on these dimensions. The particle length scale is represented by the Bohr radius, \( r_B \),

\[
r_B = \varepsilon \frac{m}{m^*} r_{\text{hydrogen}},
\]

where \( \varepsilon \) is the dielectric constant of the material, \( r_{\text{hydrogen}} \) is the Bohr radius of the hydrogen atom, and \( m^* \) is the effective mass of excited particle. This relationship applies for electrons, holes, and excitons.

Particle-in-a-Sphere Model

A first-order approximation to the size-quantized electronic properties of a semiconductor quantum dot is provided by the particle-in-a-sphere model. In this model, the quantum dot consists of a small sphere of semiconducting material is surrounded by a perfect insulator. The infinite energy gap of the insulator creates an infinite energy barrier at the surface of the sphere that confines all particles within the semiconductor. The wavefunctions of the particle within the sphere are modeled as Bloch functions, and take into account the periodic potential in the semiconductor lattice. The use of Bloch
functions results in an effective mass approximation for the valence and conduction bands in the semiconductor lattice. Solving the time-independent Schrödinger equation and accounting for the combined effects of size-quantization and the periodic potential leads to discrete allowed energies, $E_v$ and $E_c$, on the parabolic valence and conduction bands of the bulk material,

$$E_v = -\frac{\hbar^2 k^2}{2m_h}$$ \hspace{1cm} (1.2)

$$E_c = \frac{\hbar^2 k^2}{2m_e^*} + E_g$$ \hspace{1cm} (1.3)

where $E_g$ is the bulk semiconductor bandgap and $m_e^*$ and $m_h^*$ are the effective masses of electrons and holes in lattice, respectively. The allowed valence and conduction energy states are shown in Figure 1.3. Reduction of continuous energy bands to discrete allowed energies leads to the discrete emission and absorption spectra observed in quantum dots.

![Figure 1.3. Dispersion (E(k)) relation showing allowed valence and conduction energy states predicted by the particle-in-a-sphere model of the quantum dot.](image-url)
The particle-in-a-sphere model predicts an inverse-squared dependence of quantum dot bandgap, $E_{g,QD}$, on the radius of the nanocrystal $R$,

$$E_{g,QD} = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right).$$

Thus, decreasing quantum dot size leads to an increase in bandgap and a shift of photon absorption and emission maxima towards shorter wavelengths, compared to the bulk semiconductor material.

1.3.2.4 Optical Properties

The normalized absorption spectrum and normalized photoluminescent emission spectrum of ~6 nm PbS CQDs in solution shown in Figure 1.4. The absorption spectrum shows the fundamental spectral features predicted by the idealized representation of the CQD electronic structure: the fist and second excitonic absorption peaks at 1460 nm and 1050 nm. (The second excitonic absorption peak is only an inflection in the absorption spectrum of this sample.) The absorption spectrum shows significant inhomogeneous broadening due to variations in particle size and surface irregularities. Despite these non-idealities, absorption cutoff occurs at ~1800 nm – a significant and controllable spectral distance from the cutoff of bulk PbS at ~3000 nm. The photoluminescent (PL) emission spectrum has a single peak at 1575 nm. The single emission wavelength and relatively small Stokes shift indicate that near-band-edge emission is the dominant form of radiative recombination in the CQDs. A detailed discussion of photoluminescent emission from CQDs is presented in Section 6.5.
Figure 1.4. Normalized absorption spectrum and photoluminescent emission spectrum of a representative sample of PbS CQDs in solution.

1.3.4 Summary

Controlled optical and electronic characteristics, combined with solution-processing, make CQDs a very attractive medium for fabricating semiconductor photodetectors suitable for a wide range of applications. Wet chemical processing enables direct integration with a wide variety of substrates, flexible and rigid, crystalline and amorphous. PbS CQDs are particularly attractive, providing controlled absorption in the visible and IR.
1.4 Thesis Objectives

Ideally, photodetectors should be both very fast and very sensitive. The performance of previously reported CQD photodetectors has been limited to either:

- very high sensitivity and very low photoresponse speed
  - i.e. photoconductive CQD photodetectors – introduced in Section 2.2

or

- moderate photoresponse speed and very low sensitivity
  - i.e. photodiode CQD photodetectors – introduced in Section 4.1

The goal of this work is to break, for the first time, the apparent speed-sensitivity compromise in solution-processed light sensors – demonstrating sensitivity comparable to the best photodetectors fabricated from crystalline semiconductor materials (normalized detectivity > 10^{12} Jones – a figure of merit introduced in Section 2.1.3) at photoresponse speeds in excess of the fastest CQD photodetectors reported (3dB frequency > 50kHz)^2. To meet this goal will require a nearly 1000 fold improvement in the sensitivity-bandwidth product compared to the best previous works in solution-processed optoelectronics^1.

High photoresponse speed combined with high sensitivity will enable CQD photodetectors to be used in the widest possible range of applications that require direct integration of photodetectors with microelectronics or emerging technologies such as organic circuits, microfluidics, and optical circuitry.
1.5 Thesis Overview

The thesis begins with an introduction to the principles of photodetection in Chapter 2. The mechanisms of light detection and the sources of noise that limit photodetector sensitivity are reviewed. This review focuses on the two photodetection mechanisms employed in CQD photodetectors – photoconductivity and photovoltaic response. The figures of merit used to describe photodetector performance are also introduced. Based on these concepts, the operational characteristics and performance of existing photoconductive CQD photodetectors is discussed.

Chapter 3 presents the monolithic integration of photoconductive CQD detectors with silicon microelectronics to form the first known example of a CQD-sensitized imaging array. This study demonstrates the simplicity of fabricating a highly-integrated optoelectronic system with solution-processed photodetectors. These imaging arrays capture still and moving images of subjects illuminated with either visible or IR light, clearly demonstrating the extended spectral range accessible using CQD photodetectors. This study also demonstrates the serious shortcomings of photoconductive CQD photodetectors and provides the motivation for the development of fast, sensitive CQD photodetectors based on a photodiode architecture.

Chapter 4 introduces the CQD photodiode. The chapter begins by reviewing the characteristics and performance of previously reported CQD photodiodes and the fundamental limits of photodiode performance. The chapter then focuses on the CQD photodiode architecture employed in the thesis research – a Schottky barrier formed at
the junction between a metal contact and a CQD film. A quantitative physical description of the Schottky barrier is presented, based on temperature-dependent current-voltage and capacitance-voltage measurements. Models of the dark-current behaviour and junction capacitance based on bulk semiconductor theory are shown to provide good fits to measured device characteristics. This study is the first known examination of the physical structure of Schottky barriers to CQD films.

Chapter 5 discusses the development and optimization of the CQD photodiode as a photodetector. New materials processing techniques are developed to eliminate chemical reactions between device components that lead to short-circuit dark current and dark current noise in the Schottky barriers to CQD films. Elimination of this noise, and optimization of the device for high photoresponse, leads to the demonstration of record sensitivity in a CQD photodiode. This device also demonstrates photoresponse speeds equivalent to the fastest CQD photodetectors. CQD photodiode characteristics and performance are examined in detail, leading to a new understanding of device operation. The photoresponse is shown to consist of components corresponding to the drift and diffusion of photogenerated charge carriers. The capacity of this conceptual model to describe the photoresponse of the CQD photodiode is demonstrated through implementation in a numerical model.

Chapter 6 investigates charge carrier drift and diffusion in CQD films. Established measurement techniques based on field-driven charge extraction and time-of-flight are used to determine the drift mobility of majority carrier hole and minority carrier electrons
in CQD films. Diffusion of charge carriers is not well understood in CQD films, and has not been measured previously. Spectral photocurrent measurements are employed to measure minority carrier electron diffusion lengths directly in CQD photodiodes. This is the first direct measurement of charge carrier diffusion in a CQD film. The observation of increasing diffusion lengths with device exposure to ambient conditions is explained in terms of increasing carrier lifetime due to a reduction in non-radiative recombination in CQD films.

In Chapter 7, the understanding of CQD photodiode operation developed in Chapters 5 and 6 is leveraged to develop an improved CQD device architecture capable of significantly increased photoresponse speed. By reduction of the CQD film thickness, a fully-depleted CQD Schottky barrier diode is formed in which photogenerated charge is transported by drift alone. Elimination of the slow, diffusive component of the photoresponse leads to the demonstration of photoresponse speeds > 1 MHz while maintaining excellent sensitivity. The sensitivity-bandwidth of this fully-depleted CQD photodiode represents a >1000 improvement compared to the best previous works in solution-processed optoelectronics.

Chapter 8 summarizes the advances in CQD photodetector performance and CQD materials and device understanding made during the course of this research. The chapter concludes with recommendations for future work in the development of this very promising class of solution-processed optoelectronic device.
Chapter 2. Colloidal Quantum Dot Photodetectors

2.1 Photodetector Principles

An overview of the principles of operation of photodetectors is presented in the following section. Photodetector performance is determined by a combination of photoresponse – which is a function of the detection mechanism – and noise – which is determined by device architecture and the operating environment. The figures of merit used to describe photodetector performance are also discussed. This overview serves as an introduction to recently demonstrated photoconductive CQD photodetectors. A more complete treatment of photodetector principles can be found in any of several excellent reference texts\textsuperscript{10,22,23}.

2.1.1 Detection Mechanisms

Photodetectors are typically classified according to their detection mechanism. This mechanism is either photon detection or thermal detection. Photon detectors are sensitive only to photons with energy in excess of the potential energy required to generate free charge carriers, while thermal detectors absorb radiation uniformly, independent of the photon energy. Photon detectors then collect the free carriers or use free carriers to increase the conductivity of the detector material, while thermal detectors measure a change in the physical properties of the detector material in response to a change in temperature.
Photon detection is further broken down into photoemissive, photovoltaic, and photoconductive mechanisms. The photovoltaic and photoconductive photon detection mechanisms are based on the generation of free carriers within semiconductor materials by absorption of photons with energies, $E_{\text{photon}}$, equal to or greater than the semiconductor bandgap, $E_g$.

\[
E_{\text{photon}} = \frac{hc}{\lambda_c} \geq E_g .
\]  

(2.1)

This minimum energy corresponds to the detector absorption cutoff wavelength, $\lambda_p$. Photoemission, in contrast, is based on the photoelectric effect and the carrier generation process is governed by the energy required to free electrons from a metal surface. The photovoltaic and photoconductive mechanisms are the focus of CQD photodetector development, where spectral tuning of the detector is accomplished through quantum size effect control of $E_g$.

**Photovoltaic Detectors**

The photovoltaic effect is the generation of an externally measurable potential across a metallurgical junction in response to incident optical radiation. Semiconductor junctions are most commonly used to implement photovoltaic devices. The junction provides a built-in electric field for separating excess electrons and holes generated through the absorption of light by the semiconductor. Photovoltaic photodetectors produce either a voltage or current response, depending on the configuration of the external electrical circuit connected to the detector.

The current-voltage, $I-V$, characteristic of a photovoltaic detector,
is a combination of the un-illuminated $I-V$ characteristic of the junction, $i_{dark}$, represented by the diode equation, and the photogenerated current, $i_{photo}$. The photogenerated current, 

$$i_{photo} = q\eta\phi,$$  

(2.4)
is a linear function of the quantum efficiency of the detector, $\eta$, and the photon flux, $\phi$. Photovoltaic detectors are commonly operated in a current sensing (short-circuit) mode, providing a linear current response to illumination. In this mode, the detector impedance remains independent of the photon flux.

The response speed of a photodiode is determined by the time required for photogenerated carriers to be transported to the contacts. This transport time should be less than the carrier lifetimes in order maintain high quantum efficiency. The response time typically includes two components: a fast component corresponding to carrier drift within regions of the detector containing an electric field, and a slower component corresponding to carrier diffusion due to a concentration gradient in regions of the detector where no electric field is present.

**Photoconductive Detectors**

Photoconductivity is the change in conductivity of a material in response to incident optical radiation. Photoconductive detectors make use of this effect to alter device impedance in response to illumination.
The photoconductive response in semiconductor materials results from an increase in the number of free carriers available to transport current. The change in conductivity, $\Delta \sigma$, 

$$\Delta \sigma = q \Delta N \mu ,$$  \hspace{1cm} (2.5)

is proportional to the net change in the carrier concentration, $\Delta N$. The exact relationship between $\Delta N$ and the flux depends on the carrier lifetime and is strongly influenced by the presence of traps in the semiconductor. The current response of the photoconductive detector, $i_{\text{photo}}$, 

$$i_{\text{photo}} = q \eta \phi G ,$$  \hspace{1cm} (2.6)

is similar to the photovoltaic detector with an additional term accounting for photoconductive gain, $G$.

Photoconductive gain and device response time are closely linked. For devices with ohmic contacts, response time is determined by the lifetime of the photogenerated carriers. In these devices, photogenerated carriers are swept out of the device by the electric field, and are replenished at the opposite side of the device by an efficient injecting contact. This results in the possibility of more than one charge carrier traversing the device for a single carrier generation event. This phenomenon results in photoconductive gain. The gain, $G$, 

$$G = \frac{\mu E t_l}{d} ,$$  \hspace{1cm} (2.7)

is a linear function of the electric field in the semiconductor, $E$, and increases with bias. The gain is also proportional to the mobility of the free carriers, $\mu$, the carrier lifetime, $t_l$, and the distance between the electrical contacts, $d$, and can be represented as,
the ratio of carrier lifetime, to time required for carriers to transit the device, $t_{tr}$. In devices where injection of free carriers is prevented by a blocking contact, response time is determined by the transit time, and the photoconductive gain is limited to unity.

### 2.1.2 Noise Sources

The ability of a photodetector to resolve optical signals is bounded by photon noise in the signal and background illumination, and additional electrical noise generated in the detector. Total noise is cumulative, and may be dominated by one or more noise components, depending on the detector architecture and operating conditions.

#### Photon Noise

Photon noise is the lowest possible noise limit in an optical detection process and determines the ultimate sensitivity of a detector, independent of any detector properties. Photons are discrete entities that obey Poisson statistics. The instantaneous rate of photon emission from a source varies with time, resulting in a distribution of photon arrivals at a detector. The standard deviation of a Poisson distribution, $\sigma$,

$$\sigma = \sqrt{n} ,$$  \hspace{1cm} (2.9)

is equal to the square root of the mean, $\bar{n}$, of the distribution. A correction to the standard deviation to account for a distribution of photons with a range of energies that obey Bose-Einstein statistics can be made, however, this correction can be ignored for blackbody sources at practical temperatures\(^{10}\). As these photons are detected, the
variation in the arrival rate is translated into a variation in the output signal of the detector.

Photons originate from two sources, the signal and any background illumination. A well designed detection system maximizes the ratio of signal to background illumination incident on the detector. When working in the IR, detectors may be sensitive to background photons emitted by objects acting as blackbody sources. The ability to cutoff detector sensitivity to longer wavelength photons is critical for limiting this sensitivity, especially when working at or near room temperature. A detailed calculation of the effect of background photons on detector performance is presented in Section 4.2.

**Detector Noise**

The principal noise sources within photovoltaic and photoconductive detectors are thermal noise, shot noise, 1/f noise, and generation-recombination noise. These noise sources can be treated as voltage or current sources in the detector circuit model. In the context of photoconductors and photovoltaic detectors operated in short circuit mode, it is convenient to work with noise currents.

Thermal noise, also known as Johnson noise or Nyquist noise, originates from the thermal motion of charge carriers in a resistive element. It is an intrinsic noise source found in all materials. Thermal noise current, $i_t$, 

$$i_t = \frac{4k_B T \Delta f}{R_o},$$

(2.10)

is a function of the effective shunt resistance of the device, $R_o$, the temperature, $T$, the operating bandwidth, $\Delta f$, and Boltzmann’s constant, $k_B$. 

23
Shot noise originates with the discrete nature of charge carrier emission over a potential barrier, similar to the emission of photons from an optical source. Shot noise is present only in devices with a potential barrier, such as photodiodes, and is associated with both the photocurrent and dark current of the device. Shot noise is equivalent to the standard deviation of a Poisson distribution representing the arrival of the charge carriers. Shot noise current, $i_s$,

$$i_s = \sqrt{2q\bar{i}\Delta f}, \quad (2.11)$$

is proportional to the mean dc current, $\bar{i}$, and the operating bandwidth of the device, $\Delta f$. As the DC current is proportional to the cross-sectional area of the device, shot noise is proportional to the square root of this area.

$1/f$ noise is the least understood noise source, but is commonly encountered in detectors at low frequencies (<1 kHz). The source of this noise has been attributed to non-ohmic contacts and variation in the time constants of charge carrier traps that interrupt current flow in semiconductors\textsuperscript{10}. $1/f$ noise current, $i_f$,

$$i_f \propto \sqrt{\frac{\bar{i}^2}{df}}, \quad (2.12)$$

is proportional to the mean dc current, $\bar{i}$, and inversely proportional to the square root of the operating frequency, $f$. The exact dependence on frequency varies between devices and is determined empirically.

Generation-recombination noise results from statistical fluctuation in free charge carrier generation and recombination rates. These variations in these rates are attributable to the
distribution of carrier lifetimes and variation in the generation processes. Generation-
recombination noise current, $i_{gr}$,

$$i_{gr} = 2qG\sqrt{\eta \phi A \Delta f + g_{th} Ad \Delta f} ,$$  \hspace{1cm} (2.13)

is proportional to the optoelectronic gain, $G$, quantum efficiency, $\eta$, area, $A$, operating
bandwidth, $\Delta f$, thermal generation rate, $g_{th}$, and thickness of the detector, $d$. In the case of
photoconductors, the photon generation rate is typically larger than the thermal
generation rate, and its variation is tied to photon noise. The relative contribution of
generation-recombination noise in photoconductors can be very large, as it is the only
noise source dependent on the gain of the device.

**Total Noise**

The total noise observed at the output of the detector is the sum of the power of the
individual noise sources. As such, noise current sources add in quadrature,

$$i_{noise} = \sqrt{i_t^2 + i_n^2 + i_f^2 + i_{gr}^2 + \ldots} .$$  \hspace{1cm} (2.14)

The relative contribution of each of these noise sources depends on the detector
architecture and operating conditions. In the absence of illumination or applied bias, at
very low frequencies, $1/f$ noise dominates the electrical noise of photovoltaic and
photoconductive detectors. In photoconductors, with increasing frequency, GR noise
becomes dominant until, finally, only thermal noise is present\textsuperscript{22}. In photovoltaic
detectors, current noise at frequencies above the $1/f$ knee originates entirely from thermal
noise\textsuperscript{24,25}, as excess noise in the absence of an external current or illumination source
violates thermodynamic principles\textsuperscript{26}. Application of a bias introduces dark current shot
noise and moves the $1/f$ knee to higher frequencies\textsuperscript{25}. In photodiodes under bias, shot
noise, rather than thermal noise, defines the frequency-independent background noise intensity at higher frequencies\textsuperscript{25}.

### 2.1.3 Figures of merit

Figures of merit allow comparison of the performance of various types of photodetectors based on standardized, measurable characteristics. The most common figures of merit were originally developed to characterize thermal detectors and, as a result, make use of energy units, rather than photon-flux units.

The responsivity of a photodetector is the ratio of output signal per unit of incident optical power. For photodetectors operated in a current sensing mode, current responsivity, $R_i$, is the output current, $i_{out}$, per watt of optical input power, $P_{in}$,

$$R_i(\lambda, f) = \frac{i_{out}(\lambda, f)}{P_{in}},$$

in units of A.W\textsuperscript{-1}. Responsivity in photon detectors is inherently a function of the wavelength of the incident optical power, $\lambda$. Responsivity is also a function of the frequency of the illumination, as the frequency response of a photodetector is finite.

The sensitivity of a photodetector relates its ability to resolve weak optical signals. Sensitivity is characterized by the noise equivalent power, $NEP$,

$$NEP = \frac{i_n}{R_i},$$
in units of W, and is proportional to the total internal noise current, $i_n$, divided by the responsivity. The NEP is the illumination required to generate a signal with a magnitude equal to the noise of the detector. Sensitivity, in terms of NEP, is dependent on detector geometry and operating conditions, and is not suitable for comparing dissimilar detectors.

The sensitivity of photodetectors, especially IR detectors, is more commonly reported as a normalized detectivity, $D^*$,

$$D^* = \frac{\sqrt{A\Delta f}}{\text{NEP}},$$

(2.17)

in units of Jones (cm.$\sqrt{\text{Hz}.\text{W}}^{-1}$), to allow direct comparison of detectors with different active areas, $A$, and operating bandwidths, $\Delta f$.

2.2 Photoconductive CQD Photodetectors

2.2.1 Photoconductivity in CQD Films

The first devices to demonstrate the potential of CQD materials for sensitive photodetection were based on a photoconductive detection mechanism. Photoconductivity has been reported extensively in films of CQDs fabricated from a variety of semiconductors including cadmium chalcogenides (CdS, CdSe, CdTe)\textsuperscript{27-29} and lead chalcogenides (PbS, PbSe, PbTe)\textsuperscript{4,30}. These semiconductors also demonstrate photoconductivity in their bulk form\textsuperscript{31-33}. The photoresponse of CQD films based on cadmium chalcogenides is limited to visible and UV illumination as a result of the large bulk bandgap of these semiconductors (1.6 eV to 2.4 eV). Lead chalcogenides, however,
have bulk bandgaps ranging from 0.27 eV to 0.41 eV, providing CQDs based on these materials with spectrally tunable photoresponse across the UV, visible, and IR.

2.2.2 Photoconductive CQD Photodetectors

Photoconductive CQD photodetectors typically consist of a CQD film deposited over a pair of patterned metal electrodes on an insulating substrate. PbS CQD photoconductive detectors recently demonstrated remarkable sensitivities in both the IR\(^1\) and visible\(^{34}\), with \(D^*\) up to \(10^{13}\) Jones and \(>5\times10^{12}\) Jones, respectively. These sensitivities were achieved using photoconductive gains up to 2000. These devices outperformed photodetectors fabricated from conventional semiconductors in terms of sensitivity.

An inherent compromise of the photoconductive gain mechanism is slow response speed; determined by carrier lifetime. These ultrasensitive PbS CQD detectors reported 3 dB frequencies of 18 Hz and 8 Hz, consistent with the longest lived trap lifetimes of 70 ms and 125 ms\(^{1,34}\).

The photoconductive mechanism in PbS relies on the availability of minority carrier electron traps. With increasing illumination levels, these traps become full, altering the photoresponse of the device. This effect limits the linearity of the photoresponse of PbS CQD photoconductors (linearity within 10% demonstrated over only three decades of irradiance)\(^{34}\). The compression of gain at higher irradiances may, however, be useful for providing wide dynamic range response.
Ink-jet printing techniques have been used for fabricating highly reproducible, patterned arrays of CQD photoconductive photodetectors with feature sizes on the order of 100 μm\textsuperscript{17}. These devices, fabricated from HgTe CQDs, also demonstrated the longest wavelength operation of a solution-processed semiconductor device, 3000 nm. A $D^*$ of 3.2x10\textsuperscript{10} Jones was reported at 1400 nm. No temporal response characterization was provided, although $D^*$ was calculated at 10 Hz, indicating that response speed of these devices are likely similar to those reported for PbS CQDs.

Photoconductive CQD photodetector device dimensions have recently been scaled to the nanometer range\textsuperscript{35}, indicating possible applications in near-field optical detection. Fabrication of these devices is similar to that larger photodetectors: a CdSe/ZnS core-shell CQD film is deposited over pre-patterned parallel electrodes with widths of 50nm and gaps of 1.5 to 25 nm. These devices demonstrate excellent potential for dense integration due to their simple and scalable device geometry, avoiding the fabrication complexities of competing nanoscale photodetectors such as nanowires\textsuperscript{36}, nanotubes\textsuperscript{37}, single electron transistors\textsuperscript{38}, etc. The sensitivity of these devices is low, with a reported NEP of 3.7x10\textsuperscript{11} W corresponding to a $D^*$ of 8.8x10\textsuperscript{6} Jones. No temporal response characterization was reported.
2.3 Conclusions

An overview of the principles of operation of photodetectors provides the background necessary to weigh the potential advantages of the photoconductive detector architecture versus the photodiode detector architecture employed in the devices developed in later chapters of this dissertation.

Photoconductive CQD photodetectors have demonstrated exceptional performance in terms of sensitivity. However, the photoconductive gain mechanism that enables high responsivity and sensitivity also limits photoresponse speed and linearity in this class of devices. Solution-processing, combined with effective methods for patterning and demonstrated device sizes ranging from the macroscopic to a few tens of nanometers, indicates the potential for CQD photodetectors to be integrated into dense optoelectronic systems.
Chapter 3. Monolithically Integrated Photoconductive CQD Imaging Arrays

3.1 Introduction

Direct integration with silicon microelectronics to form IR sensitive imaging arrays is one of the most promising applications of photoconductive CQD photodetectors. Imaging applications can readily make use of the high sensitivity and compressed dynamic response of CQD photoconductors to enable operation over a wide range of scene illumination. Video imaging arrays operate at refresh rates of ~30 Hz – similar to the response speeds observed in CQD photoconductors. This application has the potential to exploit all of the best characteristics of these devices while avoiding their greatest limitation – operating speed.

IR imaging arrays currently make use of multiple semiconductor substrates: one for implementation of IR sensitive photodetectors, the other for signal processing electronics. These substrates are then bonded mechanically to form the complete imaging array. The size and resolution of these arrays is limited not by the photodetector or electronic circuitry, but by the size, yield, reliability, and cost of the bonds between the substrates. Substitution of a solution-processed semiconductor for the crystalline semiconductor
substrate used to implement the IR sensors would allow monolithic integration of IR sensitive imaging arrays and eliminate the restrictions of these mechanical bonds.

### 3.2 Near IR and Short Wavelength IR Imaging

The infrared spectrum is considerably broader than the visible spectrum and is subdivided into regions defined by transmittance windows in the Earth’s atmosphere:

- **near infrared (NIR):** 0.75–1.4 µm (J-band)
- **short wavelength infrared (SWIR):** 1.4–3 µm (H-band and K-band)
- **mid wavelength infrared (MWIR):** 3–8 µm
- **long wavelength infrared (LWIR):** 8–15 µm
- **far infrared (FIR):** 15–1,000 µm

The spectral range of PbS CQD photodetectors includes the near IR (NIR) and short wavelength IR (SWIR) bands in addition to the UV and visible.

Image capture in the NIR and SWIR makes use of reflected light provided by illumination sources typically separate from the subject. In reflected light imaging, image contrast results from the surface properties of the subject, yielding image features similar to those perceived by the human eye. Image capture at longer IR wavelengths makes use of light emitted by the subjects themselves, resulting in thermal images with little or no surface detail.

Imaging in the NIR and SWIR is motivated by the availability of naturally occurring illumination from the sky, even at night. The total night sky brightness results from a superposition of atmospheric and extra-terrestrial sources. The dominant source of non-
artificial, non-lunar night illumination in the NIR and SWIR wavelengths is airglow in the Earth’s upper atmosphere\textsuperscript{39}. Airglow is the result of hydroxyl group (OH\textsuperscript{-}) reactions at 90 km and atomic oxygen (OI) reactions above 150 km, however the OH\textsuperscript{-} reactions dominate for the NIR and SWIR wavelengths\textsuperscript{39}.

![Graph showing spectral radiance of total night sky illumination under new moon conditions](image)

Figure 3.1. Measured spectral radiance of total night sky illumination under new moon conditions.

Airglow is observed at terrestrial altitudes in spectral regions with atmospheric windows. The most significant windows for NIR and SWIR airglow are the J and H bands, spanning 1.0-1.35 \( \mu \text{m} \) and 1.5-1.8 \( \mu \text{m} \), respectively. There is additional airglow emission in the K band from 2.0 – 2.4 \( \mu \text{m} \), however, thermal emission from the observation equipment and the atmosphere often dominate in this spectral region. Figure 3.1 shows measured NIR and SWIR spectral radiances from the representative terrestrial observations and the background radiation of a blackbody source at 300K. The average J-band and H-band radiances, calculated from the data provided by Vatsia\textsuperscript{40}, Harrison\textsuperscript{41},
Maihara\textsuperscript{42}, Steed\textsuperscript{43}, and Littleton\textsuperscript{44}, are 5.10 nW.cm\textsuperscript{-2}.sr\textsuperscript{-1.}\mu m\textsuperscript{-1} and 8.13 nW.cm\textsuperscript{-2}.sr\textsuperscript{-1.}\mu m\textsuperscript{-1}, respectively. At wavelengths as short as 1800 nm, a thermal source at 300K (room temperature) exceeds the emissions of H-band airglow. Controlled detector absorption cutoff is critical for limiting sensitivity to background thermal sources when attempting to make use of very low intensity illumination sources such as airglow.

### 3.3 Monolithic IR Imaging Array Integration Strategy

As a proof-of-concept of the monolithic integration potential of CQD optoelectronic devices, we proposed direct integration of photoconductive PbS CQD photodetectors with commercially available image processing electronics. The image processing electronics consist of two major components: a read-out integrated circuit (ROIC) that contains all the components of an imaging array other than the photodetectors, and a support electronics package that performs all additional signal processing required to capture images from the imaging array. Use of commercial image processing electronics, rather than development of a custom solution, allowed the focus of the project to remain on photodetector development and integration, rather than microelectronics design.

A detailed examination of the physical and electrical interface between the ROIC and the pixel array was used to develop the CQD photodetector integration strategy.
3.3.1 Commercial Image Processing Electronics

The Indigo ISC9705 ROIC was selected based on commercial availability, highly configurable operating characteristics, and manufacturer support for imaging array development. This device is designed to be integrated with a photodetector array via indium bump bonding between bond pads on the ROIC surface and similar pads on the array. Figure 3.2 shows a top-view of the ROIC die. Note that the pixel interface bond pad array comprises the majority of the die area. The ISC9705 device provides 256 lines and 320 columns of resolution, for a total of 81,920 pixels, multiplexed into a single, raster-scanned, serial analog output.

![Top-view of the ISC9705 ROIC die (size: 11 mm by 11 mm).](image)

**Figure 3.2.** Top-view of the ISC9705 ROIC die (size: 11 mm by 11 mm).

**Physical Interface to Photodetectors**

Figure 3.3 shows a micrograph of a small portion of the ROIC photodetector bond pad array. Each bond pad consists of an 8 μm by 8 μm aluminium (Al) pad with a titanium
nitride (TiN) coating. The bond pad is exposed by an opening in the surface passivation dielectric. The topography of the bond pad array is not planarized. Elevation differences of up to 1.6 μm exist between the bond pad openings that lie in depressions surrounded by passivation dielectric covering the metal wires.

Figure 3.3. Micrograph of a small portion of the ISC9705 ROIC photodetector bond pad array (eight pixels shown).

**Electrical Interface to Photodetectors**

The pixel bond pads form the electrical interface between the photodetectors and the ROIC. Each detector is connected to one pixel bond pad and a common node, Vdetcom, provided by a ring of bond pads on the periphery of the pixel bond pad array. The bias
between Vdetcom and the pixel bond pads is adjustable, but is limited to -0.14 V to 9.86 V by the ROIC architecture.

![Graph showing pixel input current vs integration time for four ROIC gain modes.](image)

**Figure 3.4.** ISC9705 ROIC pixel input current minima and maxima as a function of integration time for the four ROIC gain modes.

The minimum and maximum usable pixel input current is limited by the ROIC output noise and output voltage swing, respectively. Calculated pixel input current minima and maxima as a function of integration time for the four ROIC gain modes are shown in Figure 3.4. Pixel input currents less than ~100 pA allow use of the maximum integration time and gain, while currents above this level require a reduction of integration time or gain to prevent saturation of the input. Maximum integration time and gain should lead to the highest possible sensitivity of the imaging array. The largest usable input current is ~10 nA with an integration time of 100 µs. The minimum detectable pixel current is roughly 4 orders of magnitude less than maximum pixel current throughout the range of integration time, ranging from ~1 pA to ~0.01 pA.
3.3.2 Integration Strategy

Preliminary tests showed that CQDs could be spin-cast on the surface of the ROIC while maintaining uniform film thicknesses in the bond pad openings, despite the unplanarized IC surface. These tests indicated the feasibility of direct integration of CQD films with the ROIC.

Direct deposition of the CQD film on the surface of the ROIC would allow the formation of a self-aligned array of vertically conducting photodetectors, with the position and active area of each detector defined by the aluminium ROIC bond pad forming the bottom contact. Addition of a transparent top contact would complete the structure, providing the common bias node used by the detector array. A schematic cross-section of the proposed integrated imaging array is shown in Figure 3.5. This integration strategy would eliminate the need for any patterning of the CQD film within the detector array. An adhesive mask and film lift-off is would be used to limit CQD film coverage to the pixel bond pad array, allowing direct connection of the transparent top contact to the Vdetcom bond pad ring and eliminating any external connection to the ITO film.

Figure 3.5. Schematic cross-section of the CQD sensitized FPA.
3.4 Vertical Photoconductive Photodetector Development

Aside from suitability for integration with the ROIC, the vertical CQD photodetector architecture offers both fundamental and practical advantages compared to the lateral architecture used previously\textsuperscript{1,34}. The electric field and charge carrier movement in the vertical photodetector will be normal to the CQD film surface, as opposed to parallel to the surface. This reduces the distance between the contacts, and the bias required to maintain a similar electric field in the film by approximately an order of magnitude, bringing detector operating biases into a range compatible with the ROIC. Reduction of the charge carrier path length reduces the transit time, allowing gain to be maintained in the photodetector with shorter carrier lifetimes. This has the potential to reduce the response time of the detectors. Finally, elimination of the parallel metal electrodes used in the lateral conducting detectors increases fill factor – the proportion of photosensitive area to the total detector area.

Development of vertical photoconductive detectors required a suitable transparent top contact to be integrated with the CQD film. Modification of the PbS CQD preparation was also required to reduce the photodetector dark currents to levels compatible with the ROIC pixel inputs.

3.4.1 Transparent Top Contact

Indium tin oxide (ITO) was selected for use as a transparent top contact for the CQD sensitized FPA for its relatively high conductivity, transparency in the NIR, and potential for deposition over organic thin films\textsuperscript{45-47}. A study of the effect of deposition parameters
on film characteristics allowed a reproducible procedure for low power sputtered deposition of ITO to be established (details in Appendix A).

3.4.2 CQD Synthesis and Treatment

PbS CQDs with a first excitonic absorption peak at ~1300 nm were synthesized using an oleate ligand\textsuperscript{19}. This ligand was exchanged for a shorter primary butylamine ligand via a 3-day exchange process carried out under inert conditions (details in Appendix A). The exchanged CQD solution was dispersed on the ROIC surface by spin-casting in ambient conditions. Devices were completed by depositing the transparent ITO contact over the CQD film. All devices were stored in a dry N\textsubscript{2} atmosphere after fabrication.

The established technique to sensitize the CQD films after deposition involved soaking in methanol. This had the effect to increase dark current and responsivity by close to two orders of magnitude compared to the untreated film. The resulting current density in the CQD films would produce vertical pixel detectors with ~5 nA of dark current, approximately 20x in excess of the maximum total input current of the ROIC pixel interface when configured for high-sensitivity. Several alternative processing strategies were investigated to reduce dark current in the CQD films: reducing the methanol treatment time, treating the CQDs with methanol in solution prior to film deposition, and eliminating the methanol treatment.
3.4.3 Photodetector Characterization

Photocurrent characteristics of the vertical photodetectors were obtained by fabricating test devices on ROIC bond pads used for the Vdetcom connections. These bond pads are isolated from the ROIC electronics, allowing direct electrical characterization. An LED array emitting at 1300 nm provided controllable illumination. An Agilent semiconductor parameter analyzer was used to bias and measure the dark current and photoresponse of the test pixels.

Dark Current and Photoresponse

Figure 3.6 shows dark current and responsivity as a function of bias for the differently-processed test pixels. The devices with methanol treatment after film deposition (MeOH solid) showed dark currents ~10x larger than devices with solution phase methanol treatment prior to deposition (MeOH solution) and untreated CQD films. Responsivity is also dependent on the treatment method, with a 10x difference between the solid state methanol treated and untreated films. Films with a single methanol treatment or methanol treatment during solution-processing showed comparable, intermediate responsivities, but with sublinear and superlinear dependence on bias, respectively. Methanol treatment in solution showed the best combined characteristics, having a per pixel dark current of ~ 4 pA and responsivity of 13 A.W⁻¹ for an 8 V bias.
Figure 3.6. Vertical photoconductive CQD photodetector (a) dark current and (b) responsivity as a function of bias.

**Sensitivity**

$D^*$ up to $5 \times 10^{12}$ Jones were observed in photoconductive test devices with dark currents of ~800 pA per pixel; well in excess of the requirements for integration with the ROIC. Sensitivity was observed to be proportional to responsivity and dark current. All methods used to reduce dark current also reduced responsivity and sensitivity.

**Rectification in Test Pixels**

The current-voltage characteristics of typical test pixels were symmetric, indicating ohmic junctions to the CQD film at both the Al/TiN and ITO contacts. Occasionally, strong (1000x) rectification was observed at the CQD/ITO interface. This was attributed to variation in the work function of the sputtered ITO contact. Rectification at the ITO/CQD interface reduced dark current under reverse bias. Similarly to the ohmic contacted devices, rectification also responsivity and did not yield better light/dark current ratios in the photoconductive detectors.
3.5 Photoconductive CQD Imaging Array Characterization

Complete, CQD sensitized imaging arrays were fabricated using the photodetector architecture and CQD treatment methods developed for the test pixels. The imaging arrays were connected to the commercial support electronics and fitted with a scientific camera lens to form a complete image capture system. Still and moving images were captured from the support electronics using a digital frame grabber and a composite video encoding card, respectively. All images were captured directly to a personal computer.

3.5.1 Image Capture in the Visible and IR

Initial tests of the integrated imaging array were performed using ambient, visible illumination. Figure 3.7 shows a human subject at 25 m standing in a hallway illuminated by overhead fluorescent lighting. This image is representative of subjective camera performance in terms of resolution, clarity, and uniformity. There are several obvious defects in the image. The dark horizontal and vertical lines near the top and left of the image result from documented manufacturing defects in the ROIC. The dark triangle in the upper left corner of the image is the result of partial masking-off of the photodetector array to prior to ITO deposition to exclude a CQD film defect. There are also a number of dark spots throughout the image corresponding to non-responsive individual pixels. The only image correction applied to the still images was linear photoresponse nonuniformity correction (NUC) and setting black and white saturation levels to establish image contrast. These functions were performed after image capture using MATLAB.
To ensure the photoresponse of the CQD sensitized imaging arrays was due to the CQD photodetectors, rather than photoresponse from Si p-n junctions in the pixel input circuitry of the ROIC, images were also captured using 1300 nm monochromatic illumination. The subjects in these images were clearly resolvable, however the range of image capture was limited by the illumination source output power.

Figure 3.8a shows a human subject illuminated with a combination of visible and IR light from a 150 W tungsten-halogen source. Figure 3.7b shows the same scene illuminated with an IR light from a 500 W tungsten-halogen source filtered with an Si wafer. The
mean irradiance at the subject was adjusted to be equivalent in both images. These images show the capability of the integrated imaging array to operate with similar performance across both the visible and the NIR.

![Figure 3.8](image-url)

Figure 3.8. Dr. Brad Taft illuminated with a single (a) 150 W tungsten-halogen source (3.1 mW.cm\(^{-2}\) at 950 nm) and (b) Si filtered 500 W tungsten-halogen source (3.2 mW.cm\(^{-2}\) at 1300 nm).

### 3.5.2 Imaging Array Sensitivity

Measured test pixel performance indicated that all variations of the methanol treated CQD photoconductive detector should have sufficiently low dark current for compatibility with the ROIC. In integrated imaging arrays, however, only untreated CQD films yielded useful photoresponse. These devices were used for all images shown in the previous section.
Discrepancy between Imaging Array and Test Pixel Performance

Films with average test pixel dark currents substantially greater than 1 pA typically resulted in imaging arrays with very nonuniform dark current and photoresponse. In these cases, the spatial variation of photodetector current exceeded the dynamic range of the ROIC input and prevented the use of post-capture nonuniformity correction. The discrepancy between test pixel performance and integrated device performance was attributed to the use of clusters of 50 to 150 individual pixels measured in parallel during test pixel characterization. Nonuniformity in individual pixel performance was not apparent in these measurements.

Noise Equivalent Illumination and D*

Use of untreated CQD films with reduced responsivity was expected to reduce the overall sensitivity of the integrated imaging array compared to individual photoconductive CQD photodetectors demonstrated previously. Integrated imaging array sensitivity was measured by direct illumination of the pixel array using a 1300 nm monochromatic LED illuminator. The ROIC and photodetector array were configured to provide the highest possible sensitivity through use of largest available ROIC gain and detector bias. The digitized photocurrent response of individual pixels in the array were sampled as a function of the incident irradiance. The irradiance was reduced until the pixel photoresponse reached the noise floor, yielding the noise equivalent irradiance (NEI). Two similarly processed integrated imaging arrays showed an average NEI of 2 \( \mu \text{W.cm}^{-2} \), corresponding to a photodetector D* of 3x10^9 Jones.
Subjective Sensitivity

To obtain a subjective indication of the performance of the integrated imaging array in low light conditions, images were captured of a dimly lit street at night. Figure 3.9a shows an image captured with ambient illumination and Figure 3.9b shows the same scene with additional illumination from a 500 W tungsten-halogen source filtered with an Si wafer located at the camera.

![Image](image1)

Figure 3.9. A dimly lit city street captured using (a) ambient illumination (2.4 μW.cm\(^{-2}\) centered at 950 nm) and (b) with a Si filtered 500 W tungsten-halogen source located at the camera (42 μW.cm\(^{-2}\) at 1300 nm at ~15 m).

3.6 Limitations of Photoconductive CQD Photodetectors for Imaging Applications

Integration of photoconductive CQD photodetectors with Si microelectronics illustrated the limitations of these devices in their current form.
**Dark Current and Photodetector Sensitivity**

The high dark current of photoconductive CQD photodetectors easily overwhelms the limited capacity of the current-integrating pixel inputs to the ROIC. Reduction of the detector bias or film conductivity to reduce these currents resulted in lower photodetector responsivity and sensitivity. High dark currents effectively prevented integration of the of most sensitive CQD photoconductive detectors. The best imaging arrays demonstrated $D^*$ approximately 3 orders of magnitude too low for passive SWIR imaging.

**Temporal Response**

The temporal response of the integrated imaging array, obtained from moving image video capture at 30 Hz, showed discernable lag in the photodetector response. Depending on the contrast difference, image lag lasting between less than a second, up to several seconds was apparent. The source of this lag was the long response timeconstants of the CQD photoconductive detectors.

**Spectral Response**

The first excitonic feature of the CQD used in the PD detectors is located at ~1300 nm. While this provides good coverage of the J-band NIR portion of the airglow spectrum, the CQD film is unable to absorb any of the SWIR H-band emission that comprises ~60% of the power reaching terrestrial elevations. Limited spectral absorption places additional constraints on device sensitivity for passive SWIR imaging.
3.7 Conclusions

Demonstration of large-scale integration of CQD photodetectors with Si microelectronics indicates the viability of using solution-processed semiconductors and deposition techniques for fabricating hybrid optoelectronic devices with extended spectral sensitivity and integrated signal processing. This study serves as a proof-of-concept for solution-processed photodetectors to supplant crystalline detectors in applications constrained by device integration.

Still and moving image capture was enabled by the development of a photoconductive CQD device architecture suitable for direct integration with commercial image capture electronics. Development of the vertical-transport photoconductive photodetector reduced the operating bias of the CQD photodetector to levels compatible with CMOS microelectronics. This architecture also provided maximum fill-factor in the imaging array by eliminating the electrodes used in laterally conducting detectors.

However, in their current form, PbS CQD photoconductors are not ideal for imaging applications. Foremost, the response times of these devices are too long, leading to visible artifacts in scenes with motion or changing illumination levels. High dark currents in the photoconductive detectors are incompatible with the input capacity of existing imaging electronics. The electronics could be redesigned to accommodate these currents, however the resulting arrays would consume significant amounts of power and reset noise associated with the large integration capacitors may limit sensitivity.
Development of CQD photodetectors optimized for integration with silicon microelectronics must provide faster response times (~30 μs) and lower dark currents (< 1 mA.cm⁻²). For passive SWIR applications these detectors also need to provide full spectral coverage from the visible to ~1800 nm. Further development of photoconductive devices could accomplish these goals if control over long-lived traps and film conductivity was established. Alternatively, other detector architectures based on CQDs could be developed to provide high sensitivity as well as high operating speed and minimal dark current.

This study provided an opportunity for experimental determination of the ideal requirements for photodetectors designed for highly integrated optoelectronic applications. These requirements were used to guide the development of highly sensitive, low dark-current, broadband CQD photodetectors.
Chapter 4. Development of CQD Schottky Barrier Photodiodes

4.1 Previous CQD Photodiodes

Despite the excellent sensitivity demonstrated by photoconductive CQD photodetectors, operating speeds of < 20 Hz preclude their adoption in all but niche applications. CQD photodetectors based on a photovoltaic, rather than a photoconductive architecture, have demonstrated significantly faster photoresponse.

A photodiode formed by the metallurgical junction between a 200 nm thick layer of CdSe CQDs and a conductive polymer, PEDOT:PSS, demonstrated a bandwidth of 50 kHz in response to modulated illumination at 514 nm. The response speed of this device was assumed to be limited by carrier recombination lifetime. However, this photodiode demonstrated a sensitivity of only ~10^7 Jones – approximately five orders of magnitude lower than crystalline semiconductor photodetectors.

The sensitivity of the CdSe/ PEDOT:PSS photodetector was limited, in part, by poor photocarrier generation efficiency. Zero-bias EQE at the first excitonic wavelength (560 nm) was reported at 0.13%, and increased to 15% upon application of a bias of -6 V. This corresponds to a zero bias IQE of 0.6% across the measured spectrum, increasing to
70% at -6 V bias\(^2\). Increasing IQE with reverse bias indicates that photoresponse is limited by poor carrier transport and/or insufficient built-in potential for carrier separation, as evidenced by the unstable open-circuit voltage under strong (10 mW.cm\(^{-2}\)) illumination and lack of significant rectification (< 10x). The difference between EQE and IQE, independent of bias, indicates that absorption is also limiting the photoresponse and that a greater optical density is required to make use of all available illumination.

Photodiodes based instead on Schottky barriers to CdSe CQD films showed greater potential for sensitivity, with zero bias EQEs of ~2% and ~3% at the first excitonic wavelengths (530 nm and 605 nm)\(^4\). In these devices, low workfunction Al or Ca contacts to 200 nm thick CQD films provided the built-in potential for separating photogenerated carriers. Good photoresponse linearity was observed over 3 decades of illumination. Although extensive measurements of dark current relaxation and persistent photoconductivity are presented in this study, no description of the temporal response of the detector to modulated illumination at zero bias was reported. The photoresponse of these photodiodes was likely limited by low minority carrier hole mobilities (10\(^{-12}\) cm\(^2\).V\(^{-1}\).s\(^{-1}\) vs. 10\(^{-4}\) to 10\(^{-6}\) cm\(^2\).V\(^{-1}\).s\(^{-1}\) for electrons).

The low zero-bias EQE in reported CQD photodiodes indicates the potential for dramatic improvements in CQD photodiode sensitivity. Zero-bias EQE is critical for determining the sensitivity of a photodiode: in typical photodiodes, sensitivity is highest at zero bias when dark current noise sources are eliminated.
4.2 Ultimate Detectivity of CQD Photodiodes

4.2.1 Introduction

The primary advantage of photoconductive photodetectors is an intrinsic capacity for photoconductive gain\textsuperscript{48}. Gain allows these devices to achieve very high sensitivities by acting as a built-in amplification mechanism that improves the ratio of signal to fixed noise sources. The most sensitive PbS CQD photoconductive detectors have approached fundamental noise limits within 3 dB\textsuperscript{1}.

To ensure that CQD photodiodes could theoretically achieve sensitivities comparable to their photoconductive counterparts, and to devices fabricated from crystalline semiconductor materials, detailed calculations of projected performance were performed. These calculations determine a theoretical sensitivity limit based on an assumed photoconversion efficiency and the expected contribution of noise due to background thermal (blackbody) radiation and internal thermal noise generation as a function of the zero-bias impedance of the detector.

A PbS CQD photodiode was assumed to have a 1625 nm excitonic peak (~1800 nm cut-off) and 15% EQE at the peak wavelength. This excitonic peak location corresponds to the optimum location for absorption of airglow for potential applications in passive SWIR imaging. A PbS bulk photodiode was assumed to have a 3024 nm cut-off, corresponding to a bulk energy bandgap of 0.41 eV, and 55% EQE.
Further assumptions common to both detectors are as follows:

- unobstructed, spherical \((4\pi \text{ stradian})\) exposure of the detector to background thermal photon sources
- \(5 \times 10^{-3} \text{ cm}^2\) detector area (0.08 cm detector diameter)
- detector and surroundings at room temperature (300K)
- zero bias operation

### 4.2.2 Background Thermal Photon Noise Current

**PbS CQD Absorption and Responsivity Model**

The sensitivity of a photodetector to background thermal radiation depends directly on location and shape of its absorption cut-off. In CQD films, the location and shape of the first excitonic absorption feature determines these properties. Figure 4.1a shows the normalized IR absorption spectra of a representative batch of CQDs. The spectral absorption profile of the first excitonic absorption peak can be well-approximated using a Gaussian distribution, as shown in Figure 4.1a. This distribution is represented by a mean wavelength and full-width half-maximum (FWHM). An analysis of four identically synthesized CQD batches revealed an average excitonic feature located at 1630 nm with a 290 nm FWHM.
Figure 4.1. (a) Normalized IR absorption spectra of a representative PbS CQD sample: 1645 nm first excitonic peak with 280 nm FWHM. (b) Estimated spectral responsivity of the first excitonic absorption feature of a PbS CQD photodiode with 15% EQE at the excitonic peak.

The photodiode spectral responsivity corresponding to the first excitonic absorption feature is estimated by mapping the shape of the normalized absorption feature to an EQE of 15% at the absorption peak, based on the spectral dependence of photon energy, $E_{\text{photon}}$,

$$E_{\text{photon}} = \frac{hc}{\lambda}. \quad (4.1)$$

Figure 4.1b shows the resulting spectral responsivity curve. Responsivity at shorter wavelengths is not captured by this curve, but is not necessary to accurately calculate photocurrent due to absorption of blackbody radiation centered at much larger wavelengths.
PbS Bulk Absorption Model

The spectral responsivity of bulk PbS was calculated from an EQE of 55%, based on the spectral dependence of photon energy, as shown in Figure 4.2.

![Figure 4.2. Estimated spectral responsivity of a bulk PbS photodiode with 55% EQE.](image)

Background Thermal Photon Radiance and Photocurrent

The background thermal photon spectral radiance, $L_B$, in units of watt.cm$^{-2}$.sr$^{-1}$.μm$^{-1}$, is calculated from the Planck’s equation$^{10}$,

$$L_B(\lambda, T) = \frac{2hc^2}{\lambda^5(e^{hc/\lambda kT} - 1)} \tag{4.2}$$

based on the temperature of the blackbody source, $T$. Multiplying this radiance by the field of view of the detector, $4\pi$, the detector area, $A$, and the spectral responsivity of the detector, $R$, yields the spectral photocurrent generated by background thermal photons, $I_B$,

$$I_B(\lambda) = L_B(\lambda, T) \cdot A \cdot 4\pi \cdot R(\lambda) \tag{4.3}$$

The spectral photocurrent tracks the shape of the spectral responsivity of the detector, but is shifted ~200 nm toward the IR by the strong wavelength dependence of the
background thermal spectral irradiance, as shown in Figure 4.3a. Integrating over the range of absorption of the detector, yields the total photocurrent generated by background thermal photons, $I_{BT}$,

$$I_{BT} = \int I_b(\lambda) d\lambda. \quad (4.4)$$

Figure 4.3. (a) Spectral photocurrent generated by background thermal photons in the CQD photodiode. (b) Background thermal photon noise current in the CQD photodiode as a function of first excitonic absorption feature location.

**Background Thermal Photon Noise Current**

The noise current associated with the background thermal photocurrent is calculated from the shot noise model (Section 2.1.2), and is proportional to the square of the photocurrent. Assuming a CQD photodiode first excitonic absorption feature located at 1625 nm, the thermal background photocurrent noise is $0.87 \text{ fA.Hz}^{-0.5}$. For the bulk PbS detector the photocurrent noise is $190 \text{ fA.Hz}^{-0.5}$, approximately two orders of magnitude greater than in the absorption limited CQD device. The background thermal photon noise current
depends superlinearly on the location of the first excitonic absorption peak, as shown in Figure 4.3b.

### 4.2.3 Internal Thermal Noise Current

Assuming zero bias operation, internal noise within the detector is limited to thermal (Johnson) noise (Section 2.1.2), and is proportional to the square of the effective shunt resistance of the device, $R_o$.

### 4.2.4 Detector Sensitivity

Noise equivalent power, $NEP$, and normalized detectivity, $D^*$, are calculated from the predicted responsivity and total noise current in the CQD and bulk PbS photodiodes as a function of $R_o$, as shown in Figure 4.4. Both detectors are limited by internal thermal noise at low values of $R_o$. In this regime, the bulk PbS photodiode is ~4x more sensitive than the CQD photodiode at a given value of $R_o$, owing to the higher EQE of the bulk device. The transition to background thermal photon limited (BLIP) operation occurs at $\sim 10^6 \, \Omega$ and $\sim 10^{10} \, \Omega$ in the bulk and CQD PbS detectors, respectively. The onset of background limited operation is highly dependent on the cut-off wavelength of the detectors. By reducing sensitivity to background thermal photons, the CQD detector has the potential to significantly exceed the sensitivity of the bulk detector, even with a lower EQE, as $R_o$ is increased. The difference in sensitivity to background thermal photons between the CQD and bulk PbS photodetectors clearly demonstrates the benefit of controlled spectral cutoff.
A background limited normalized detectivity in excess of $10^{13}$ Jones indicates the potential for the development of highly sensitive PbS CQD photodiodes. Even with modest EQE, these devices have the potential to rival the sensitivity of IR photodetectors implemented in crystalline semiconductor materials.

![Figure 4.4](image.png)

Figure 4.4. $D^*$ as a function of effective shunt resistance for bulk PbS and PbS CQD photodiodes.

### 4.3 Development of CQD Photodiodes

#### 4.3.1 Photodiodes vs. Photoconductors

Photodiodes generally respond faster to changes in illumination than photoconductors. Response time in photodiodes is limited by the carrier transport time, rather than carrier lifetime which may persist for up to tens of milliseconds in materials with long-lived traps. Additionally, photodiodes are generally preferred over photoconductors for...
integration with microelectronic read-out circuitry, as they demonstrate low to zero dark currents, high impedance, and low power dissipation\textsuperscript{23,48}.

In this work, we took the view that reliance on the long-lived minority carrier traps essential to photoconduction would necessarily lead to slow photoresponse speeds: we therefore pursued the charge-separating photovoltaic detector architecture. However, we recognized than an orders-of-magnitude improvement in sensitivity would be required. We believed that – if guided by a detailed physical model of device operation – careful nanoscale optimization of the CQD film to provide efficient carrier transport and a metallurgical junction with a large built-in potential could potentially lead to the desired combination of sensitivity and speed.

A photovoltaic detector provides an additional degree of freedom in device design compared to photoconductive detectors: photoresponse is due to the properties of the semiconductor material \textit{and} the metallurgical junction that provides the built-in potential for carrier separation. Rather than relying solely on modification of the chemical and physical properties of the semiconductor to control the photoresponse and noise – the case in photoconductor development – device architecture becomes a central element of photovoltaic device design.

\subsection{4.3.2 Metallurgical Junctions to CQD Films}

Metallurgical junctions in semiconductors include doped homojunctions, heterojunctions, and Schottky barriers. The advantages and disadvantages, theoretical and practical, of
each of these junction types was considered in order to determine the best architectural candidate for fabricating fast, sensitive CQD photodiodes.

The p-n junction is a homojunction implemented in a single type of semiconductor. Typically, two types of dopants are distributed in adjacent regions to provide a potential difference in both the conduction and valence bands across the junction. An inherent compromise in photodiodes fabricated from p-n junctions is that low doping levels are required to provide a wide junction for efficient photocarrier capture but also limit the built-in potential of the junction\textsuperscript{49}. While doping of crystalline semiconductors is very well established, solid-state doping of CQD films was in its infancy at the outset of the CQD photodetector device architecture investigation\textsuperscript{50}. Implementation of a doped homojunction in lead chalcogenide CQDs would require significant materials and processing development.

An alternative to a metallurgical junction derived from doping a single type of CQD is a heterojunction between dissimilar types of CQDs. This type of junction is far less constrained in solution-processed semiconductors than in crystalline semiconductor materials where lattice matching requirements must be met. However, a heterojunction would require the development and optimization of two types of CQD films. PbSe and PbTe were identified as suitable counterparts to PbS to form a type-II heterojunction for charge carrier separation\textsuperscript{51}. The synthesis and surface passivation of PbSe and PbTe CQDs is similar to that of PbS\textsuperscript{52}, and would likely require only derivative changes to
established materials processing techniques to provide suitable control over film morphology, carrier mobility, and other film properties.

A Schottky barrier develops a built-in potential based on the difference in work functions between a semiconductor and metal contact. It can effectively be considered one half of a semiconductor heterojunction where one semiconductor phase is replaced by a metal. A Schottky barrier to a semiconductor film requires the development of only a single semiconductor material, however it is more sensitive to effects of interface states which can significantly alter the energy band alignment at the metallurgical junction\textsuperscript{49,53}. Compared to p-n junction diodes, Schottky barrier diodes can have higher saturation currents, resulting in lower impedance and higher dark current\textsuperscript{48}. The thermionic emission process in Schottky barriers is more efficient that the diffusion process typically limiting in p-n junction devices. Therefore, for the same built-in potential, the saturation current in a Schottky junction will be several orders of magnitude greater than that of a p-n junction. However, Schottky barrier devices have higher response speed than p-n junction diodes\textsuperscript{23}, as they are not limited by diffusion capacitance resulting from minority carrier transport in the neutral regions of the device\textsuperscript{48}.

Schottky barriers were selected to provide the metallurgical junction required for the CQD photodiode. Schottky barriers, already observed experimentally at the interface between PbS CQDs and sputtered ITO, provide the simplest route to the formation of a built-in potential in PbS CQD films. Fabrication and characterization of effective
Schottky barriers to CQD films was undertaken as the first phase of development of CQD photodiodes.

Photodetectors implemented with Schottky barriers to CQD films are photovoltaic devices. The photogeneration process in these devices is not to be confused with photoemissive Schottky barrier devices, such as far-IR photodetectors. The properties of photoemissive detectors are not derived directly from the bandgap of the semiconductor, and this architecture would not take advantage of the spectral tunability of the CQD film.

### 4.4 Schottky Barriers to CQD films

#### 4.4.1 Introduction

Previous studies of metallurgical junctions to CQDs include PbS/porous oxide heterojunctions\textsuperscript{54,55} and a single-nanocrystal Schottky junction\textsuperscript{56}. Metal colloidal nanoparticle films have also been studied in combination with a conventional, bulk crystalline semiconductor\textsuperscript{57}. The current study focused instead on a detailed investigation of the canonical Schottky barrier: a planar junction between a semiconductor and a metal contact. In this case, the semiconductor consists of a monodispersed colloidal semiconductor film. Although the PbS CQD film is composed of inorganic semiconductor particles and organic insulating molecules, it is considered to be homogeneous in its macroscopically observable electronic properties.

A previous report of a Schottky barrier to a film of CdSe CQDs focused on current-voltage characteristics as a function of materials parameters and temperature\textsuperscript{4}. This
report provided one of the first descriptions of a Schottky barrier to a CQD film. Strong rectification, dependent on the choice of contact material, was observed, as was space-charge limited current and persistent photoconductivity in the CQD film. This report, however, did not provide a full physical description of the energy band structure of these devices.

A more detailed study, focused on PbS CQDs, was necessary to gain insight into the physical and electronic structure of Schottky barriers to CQD films. The current study employed capacitance-voltage (C-V) and temperature-dependent current-voltage measurements (I-V) to determine the key parameters of the Schottky barrier – barrier height, built-in potential, and depletion width – in this materials system. These measurements support a model of device operation wherein hole current flows over a potential barrier in the valence band at the CQD-metal interface.

4.4.2 CQD Synthesis and Device Fabrication

We synthesized PbS CQDs\textsuperscript{58} capped with 2.5 nm long oleate ligands. The ligands provide colloidal stability and passivate the nanocrystal surfaces. To reduce inter-particle spacing in films and improve carrier transport, the original ligands were partially exchanged in favor of shorter primary butylamine ligands (details in Appendix A)\textsuperscript{1}. Films (250 nm-thick) were formed by spin-coating CQDs suspended in octane onto commercial glass substrates coated with conductive indium-tin oxide (ITO). Aluminum contacts (100 nm thick, 3.14 mm\textsuperscript{2} area) were deposited on top of this film by thermal evaporation at \(~\text{10}^{-5}\) Torr. A schematic representation of the Al/PbS CQD Schottky
barrier device architecture is shown in Figure 4.5. All CQD synthesis, processing, and film deposition were carried out in an inert environment with a brief (< 30 second) exposure to ambient conditions during transfer to the vacuum system for metal contact deposition. All measurements were performed in the dark with $I-V$ characterization in an N$_2$ atmosphere and $C-V$ characterization at room temperature in air.

Figure 4.5. Schematic view of the CQD Schottky barrier diode architecture.

### 4.4.3 Current-Voltage Characteristics

Figure 4.6a shows the $I-V$ characteristics of an Al/PbS CQD Schottky barrier device at temperatures from 150 K to 300 K. Strong rectification was observed at all temperatures. The exponential portion of the forward-bias $I-V$ characteristic (e.g. 0.0 to 0.3 V at 300 K or 0.2 to 0.3 V at 150 K) is well-described a simple diode equation,

$$ J = J_s \left( \exp \left( \frac{qV}{nk_B T} \right) - 1 \right), $$

where $J_s$ is the saturation current density, $q$ is the electronic charge, $V$ is the potential drop across the junction, $n$ is the ideality factor, $k_B$ is Boltzmann’s constant, and $T$ is the temperature. $J_s$ and $n$ obtained from fitting Equation (4.5) to measured $I-V$ characteristics at 300 K for three CQD Schottky barrier devices are provided in Table 4.1. Example fits of Equation (4.5) to measured data at temperatures of 150 K to 300 K are included in Figure 4.6a.
The saturation current density in Schottky barrier devices is conventionally described within one of two models: thermionic emission theory, which assumes that the carrier populations are at equilibrium throughout the depletion region and that the current-limiting process is the emission of carriers over the energy barrier; and the diffusion theory of emission, which assumes that current is limited by classical carrier transport in the depletion region rather than the emission process\textsuperscript{53}. Both theories describe an exponential dependence of $J_s$ on the Schottky barrier height ($\phi_b$) and temperature, allowing direct extraction of $\phi_b$ from temperature-dependent $I$-$V$ measurements.

We used known or estimated materials parameters to predict $J_s$ within each model and found that the diffusion model provided good agreement with the experimentally observed $J_s$, while the thermionic emission model predicted $J_s$ five orders of magnitude greater than what we observed. This finding is consistent with reports in which Schottky
barriers formed using other low-mobility semiconductors, such as polymers, are found to fit best to a diffusion model\textsuperscript{60,61}. The reverse-bias characteristics of the CQD Schottky barrier are also better-described by the diffusion theory, as the field in the depletion region is dependent on applied bias, resulting in non-saturating reverse-bias currents\textsuperscript{53}.

As shown in Figure 4.6a, at 300 K, in forward bias up to \(~0.3\) V, the $I-V$ characteristics of the Schottky barrier device are well-described by the simple diode model. At higher biases, a roll-off from the exponential $I-V$ relationship is attributable to series resistance in the bulk of the semiconductor and contacts. The reverse-bias current shows non-saturating behavior with a magnitude that exceeds the diode saturation current by ten-fold at -1.0 V. At low temperatures, the magnitude of the thermionic forward-bias current is reduced, revealing the non-saturating currents contributing symmetrically to both forward and reverse current (e.g. -1.0 to 0.2 V at 150 K) at magnitudes up to a million-fold greater than the saturation current associated with the simple diode model. These currents may be attributable to leakage through the Schottky barrier due to inhomogeneities in barrier height and width\textsuperscript{62-64}.

At low temperatures and low forward biases, small area, low-barrier-height regions contribute significantly to the forward bias current as thermal emission over the larger-area nominal-barrier-height regions is reduced. Due to the small area of the low-barrier-height regions, series resistance effects are observable at lower biases, resulting in plateaus in the forward current before contributions from the large-area, nominal-barrier-height regions again dominate as bias increases. Observation of these plateaus is
consistent with reports of barrier height inhomogeneity in lightly doped semiconductors with depletion widths of 100 nm to 1000 nm$^{64}$.

We varied the contact materials on both sides of the CQD film in order to identify the source of the asymmetric $I-V$ characteristics. Only when Al was used as one contact, and either ITO or Au used as the other contact, did we observe strong (>10x) rectification. The use of two Au or ITO contacts led to linear $I-V$; and of two Al contacts to highly nonlinear (thresholded) symmetric behavior. Owing to the high ratio of hole-to-electron mobility in PbS CQD films (as attested by their large photoconductive gain)$^{65,66}$, electron injection at the Al contact is assumed to be negligible. We conclude that the Al/PbS CQD junction forms the Schottky barrier for hole transport, and that the other junction provides an ohmic contact to the valence band.

We extracted $\phi_s$ by fitting $J_s$ to the exponential regions of the measured $I-V$ characteristics at temperatures from 150 K to 300 K, as shown in Figure 4.6a. The Schottky barrier heights extracted thereby are shown for three devices in Table 4.1. As expected, the Schottky barrier heights obtained in the present study of quantum-confined materials are larger than those reported for bulk lead chalcogenide Schottky barriers$^{67,68}$ – consistent with the larger bandgap of the CQDs. The ideality factors for the Al/PbS CQD Schottky devices (~1.3) are closer to unity than in bulk lead chalcogenide Schottky barriers (1.6 to 1.9)$^{68}$. These trends are consistent with the view that the use of short passivating ligands is effective in minimizing recombination, tunneling, and inhomogeneities$^{64}$ at the metal-semiconductor interface.
4.4.4 Capacitance-Voltage Characteristics

We employed C-V analysis to obtain the depletion region width and the exposed acceptor density near the Schottky barrier. The junction capacitance is calculated from the depletion approximation\textsuperscript{53},

\[
\frac{1}{C^2} = \frac{2}{A^2 q \varepsilon N_a} \left( V_{bi} - \frac{k_B T}{q} - V \right),
\]

(4.6)

where $A$ is the device area, $V$ is the applied bias, and $\varepsilon$ is the static permittivity of the semiconductor. Extraction of the acceptor density ($N_a$) and the built-in potential ($V_{bi}$) is achieved by fitting Equation (4.6) to the measured capacitance over a range of applied biases using a known static dielectric permittivity. The static permittivity of the PbS CQD film was obtained from Schottky barrier devices using the carrier-extraction-by-linearly-increasing-voltage (CELIV) technique\textsuperscript{69}. Application of a short-duration, linearly-increasing reverse bias to a semiconductor with a blocking contact results in drift and displacement currents, which are distinct and separable. The permittivity of the semiconductor is calculated from the displacement current, which is proportional to the device capacitance, and the geometry of the sample. Measurement of CQD Schottky barrier devices fabricated with a selection of CQD batches yielded a static relative permittivity of $17 \pm 2$\textsuperscript{70}. We show in Figure 4.7 the measured capacitance as a function of applied bias for three Al/PbS CQD Schottky barrier devices. Extracted values of $V_{bi}$ and $N_a$ for these devices are provided in Table 4.1. These charge densities are similar to trap densities calculated in CdSe CQD films through analysis of space-charge limited current\textsuperscript{4}. We also tabulate the depletion width at zero bias ($w$).
Figure 4.7. Measured capacitance as a function of bias (C-V) for Samples A, B, and C. Measurements were performed with a 10 mV probe signal modulated at 20 Hz. Reproduced with permission from59. Copyright 2007 American Institute of Physics.

4.4.5 Materials and Processing Dependencies

The three Schottky barrier devices considered in this study share a common architecture but employ two different CQD processing parameters. Both involve precipitation using methanol followed by redispersion in toluene prior to ligand exchange. For samples A and C, the precipitate-and-redisperse procedure is followed three times prior to ligand exchange; for sample B it is done only once. Time-of-flight measurements reveal a 10-fold increase in mobility in films of CQDs when three precipitations are used instead of one. In the CQD Schottky barrier devices, increased mobility is manifested in a similar increase in saturation current. The height of the Schottky barrier and the rectification ratio were not significantly affected by these very different processing steps; however $N_a$ is approximately two times larger in the triple-precipitated samples, indicating that passivating ligands on the surfaces of the CQDs are removed or made less stable by the additional methanol exposure, leading to the formation of acceptor states resulting from oxidation of PbS\textsuperscript{1,31}. 
4.4.6 Energy Bands

We summarize in Figure 4.8 our interpretation of the energetic relationship between the semiconducting PbS CQD film and the metal contact. Figure 4.8a shows locations of the energy bands of the isolated CQD film and the work function ($q\phi_m$) of metallic aluminum (4.1 eV). We situate the conduction and valence band edges in the CQD film based on a bulk PbS electron affinity ($\chi$) of 4.6 eV$^{71,72}$ and assume equal displacement of both bands due to quantum confinement in a semiconductor with equal electron and hole effective masses$^{73}$. The CQD film is treated as a homogeneous medium, consistent with the smooth, continuous macroscopic electronic properties observed in the CQD Schottky barrier devices.

Figure 4.8. (a) Valence ($E_v$) and conduction ($E_c$) bands of the isolated PbS CQD film (calculated from the electron affinity ($\chi$) of bulk PbS and the energy gap ($E_g$) of the CQD film) and the Fermi energy ($E_F$) of the Al contact (located by the metal work function ($q\phi_m$)). The inset shows a schematic view of the Al/PbS CQD Schottky barrier device architecture. (b) Energy bands near the Al/PbS CQD Schottky barrier at zero applied bias (the potential energy scale applies only to the neutral region of the PbS CQD film). See Table 4.1 for a description of the Schottky barrier parameters. Reproduced with permission from$^{59}$. Copyright 2007 American Institute of Physics.
Figure 4.8b shows the proposed energy bands in the vicinity of the Al/PbS CQD junction at thermal equilibrium and zero applied bias. The height of the Schottky barrier is predicted within Schottky-Mott theory to be ~1.0 eV based on the calculated difference in work functions of the two materials\textsuperscript{53}; however, the barrier heights extracted experimentally herein are ~0.4 eV. We account for the additional potential drop across the junction ($V_{\text{int}}$) by positing a thin interfacial layer at the junction and localized charge on the surface of the semiconductor per the Bardeen Schottky barrier model\textsuperscript{53}. The magnitude of $V_{\text{int}}$ depends directly on $\chi_s$ and may be smaller for PbS surfaces free of oxidation\textsuperscript{72}.

Within the spatial energy band diagram of Figure 4.8b it is possible to check for self-consistency by calculating the distance between the Fermi energy and the valence band edge ($E_v-E_F$) based on two methods: solving $E_F$ for charge neutrality ($p_0 = N_a$) far from the junction, or taking $E_F = E_v - qV_{\text{bi}} + q\phi_h$. For each of the samples of Table 4.1, the location of the calculated Fermi energies agreed within ~0.05 eV.

Table 4.1. Al/PbS CQD Schottky barrier parameters. Reproduced with permission from\textsuperscript{59}. Copyright 2007 American Institute of Physics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi_h$ [eV]</th>
<th>$J_s$ [A cm$^{-2}$]</th>
<th>$n$</th>
<th>Rect.</th>
<th>$V_{\text{bi}}$ [V]</th>
<th>$N_a$ [cm$^{-3}$]</th>
<th>$w$ [nm]</th>
<th>$E_g$ [eV]</th>
<th>$V_{\text{int}}$ [eV]</th>
<th>$E_v-E_F$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.38</td>
<td>1.7x10$^{-6}$</td>
<td>1.32</td>
<td>1.1x10$^4$</td>
<td>0.31</td>
<td>7.1x10$^{16}$</td>
<td>90</td>
<td>0.73</td>
<td>0.66</td>
<td>-0.07</td>
</tr>
<tr>
<td>B</td>
<td>0.38</td>
<td>1.1x10$^{-7}$</td>
<td>1.28</td>
<td>2.1x10$^4$</td>
<td>0.28</td>
<td>2.1x10$^{16}$</td>
<td>150</td>
<td>0.80</td>
<td>0.63</td>
<td>-0.10</td>
</tr>
<tr>
<td>C</td>
<td>0.40</td>
<td>1.0x10$^{-6}$</td>
<td>1.35</td>
<td>1.8x10$^4$</td>
<td>0.33</td>
<td>3.6x10$^{16}$</td>
<td>120</td>
<td>0.80</td>
<td>0.65</td>
<td>-0.06</td>
</tr>
</tbody>
</table>
4.5 Conclusions

The projected performance of photodiodes fabricated from CQD films indicates that a photovoltaic detector architecture has the potential to provide excellent sensitivity while eliminating the large dark currents and slow response of photoconductive CQD detectors. The low EQE of CQD photodiodes demonstrated to date indicates the potential for substantial improvements in photoconversion efficiency of this class of device.

Owing to its simplicity, a Schottky barrier was selected to provide the built-in potential for charge separation in PbS CQD photodiodes. An experimental study of Schottky barriers formed at the junction between a metallic contact and a semiconducting colloidal quantum dot film revealed a quantitative physical picture of structure and operation of these devices. A combination of temperature-dependent current-voltage and capacitance-voltage measurements were used to extract the key parameters of the junction: a large potential barrier, a depletion region, and an energy band structure similar to that encountered in bulk semiconductor Schottky junctions. These measurements support a model of device operation based on hole transport restricted by a potential barrier in the valence band at the metallurgical junction.

This study is the first known examination of the physical structure of Schottky barriers to CQD films.
Chapter 5. CQD Schottky Barrier Photodiodes

5.1 Introduction

Photoconductive CQD photodetectors have achieved very high sensitivity through the use slow-responding gain mechanisms and their photoresponse speeds have been limited accordingly. Photovoltaic CQD photodetectors have shown the capacity for fast photoresponse speed but have been limited by low sensitivity.

Herein we show for the first time experimentally that there exists no fundamental compromise between speed and sensitivity in CQD photodetectors. Utilizing a Schottky barrier to a CQD film to provide a metallurgical junction with a built-in potential, we develop fast-responding CQD photodiode photodetectors with very high sensitivity across the IR and visible.

5.2 Device and Materials Development Strategy

Highly-sensitive photodiodes require efficient transport of photogenerated charge carriers on length scales comparable to the absorption length of light the semiconductor material. This allows the largest possible portion of incident photons to be absorbed, converted to charge carriers, and collected at the electrical contacts before the photogenerated
electrons and holes recombine. Highly-sensitive photodiodes also require a large built-in potential for efficient charge carrier separation and suppression of noise that would otherwise limit sensitivity.

Achieving these requirements requires a semiconductor material with high conductivity (via high mobility) and sufficient passivation for forming metallurgical junctions with minimal interfacial effects. Any other materials used to form the metallurgical junction must be chemically and structurally compatible with this semiconductor material in order to minimize interfacial effects.

**Adjustment of Electronic Properties of CQD Films through Surface Modification**

A fundamental advantage of inorganic-organic hybrid CQD materials is the ability to adjust the macroscopic electronic properties of films through CQD surface modification. CQD films offer a number of chemically-tunable degrees of freedom linked to the organic molecules used to passivate their surfaces and the degree of oxidation of the CQD surface.

The spacing between individual CQDs is controlled by the length of the organic ligands used to passivate their surfaces. This has been shown to be a determining factor in the conductivity of CQD films\(^2,28,74\): inter-dot spacing controls the likelihood of individual charge carriers moving between adjacent CQDs, in turn determining their overall mobility.
The consistency of surface passivation is also important, as this limits oxidation and other chemical modification of the CQD surface. Oxidation provides a route to effectively dope a CQD film; however, uncontrolled variation in the CQD surface leads to interface states and a reduction of the built-in potential when forming metallurgical junctions. In diodes, the energetic barrier associated with the metallurgical junction defines the effective shunt resistance ($R_o$), which, in turn, determines noise performance. Thus, this interfacial control is essential for fabricating high sensitivity photodiodes.

In sum, control over sensitivity and speed of the photodiode derives directly from engineering of CQD film properties.

### 5.3 Photodiode Architecture

The metallurgical junction for the CQD photodiode is provided by a Schottky barrier to a CQD film. The Schottky barrier is formed at the interface between the PbS CQD film and an aluminum contact (Figure 5.1a). A planar, transparent ITO thin film formed the opposing ohmic contact. Light incident through the glass substrate generates electrons and holes in CQD film that are collected at the Al and ITO contacts, respectively.

The energy band diagram in Figure 5.1b shows the Schottky barrier formed at the Al/PbS CQD interface, and the built-in potential, $V_{bi}$, derived from the difference in work function between the CQDs and the metal contact. Charge transfer between the semiconductor and the metal results in the formation of a wide depletion region in the
CQD film, while the remaining volume of CQD film is a quasi-neutral region of p-type semiconductor with no net charge or electric field\textsuperscript{59}. The large potential barrier in the valence band limits majority carrier (hole) injection from the Al contact, resulting in highly rectifying dark \textit{I-V} characteristics\textsuperscript{59}.

(a)  
(b)  
Figure 5.1. (a) Schematic, cross-sectional representation of the CQD Schottky barrier diode architecture. (b) The Schottky barrier at the Al/PbS CQD interface forms a depletion region (DR) in the CQD film with a bias dependent width ($w_{DR}$) and a built in potential ($V_{bi}$). The remaining CQD film is unaffected by the Schottky barrier and is denoted as a quasi-neutral region (QNR).

5.4 Well-Passivated, High-Mobility CQD Films

5.4.1 CQD Synthesis

We synthesized PbS CQDs with a diameter of ~6 nm, increasing the effective bandgap from the bulk PbS value of 0.42 eV to 0.86 eV through the quantum size effect\textsuperscript{21}. This bandgap corresponds to a ground-state excitonic absorption feature at 1450 nm. As
synthesized, the CQDs were capped with 2.5 nm long oleate ligands\cite{19}, which provided colloidal stability and passivated the nanocrystal surfaces (details in Appendix A).

### 5.4.2 CQD Film Treatment

A three-stage CQD surface modification strategy was employed to create films of densely packed CQDs with stable surface passivation and controlled effective doping. Prior to film formation, we exchanged the original oleate ligands in favor of shorter primary butylamine (PBA) ligands in order to reduce interparticle spacing. Reduction of the ligand volume prior to CQD film formation prevents the cracking encountered when making significant changes to ligand volume in solid films. However, primary butylamine is volatile and is known to react with white metals such as aluminum. This reaction was identified as the source of dark short-circuit currents and a very short device lifetimes in early CQD photodiode prototypes resulting from corrosion of the Al contact. Benzenedithiol (BDT) forms strong bonds with PbS CQDs, and was selected to replace the primary butylamine ligands after film formation. BDT, a bidendate linker, is expected to improve film stability\cite{75} and provides an interdot spacing similar to that of primary butylamine. BDT’s thiol endgroup chemically reduces the surface of PbS CQDs. This reduction suppresses the effective doping and p-type semiconductor characteristics derived from the oxidation of PbS\cite{31}, and thus diminishes the built-in potential of the Schottky barrier from which diode behavior originates. As a final step, a re-oxidation of the CQD film was performed to return the degree of effective doping required for creating Schottky barriers with a large built-in potential and energy barrier\cite{59}.
5.4.3 Elimination of Butylamine

BDT treatment of the CQD films increased photodiode lifetime from approximately 4 hours to greater than 2 months and dramatically reduced short-circuit dark current densities from \(\sim 100 \text{ nA.cm}^{-2}\) to below \(0.1 \text{ nA.cm}^{-2}\). The 1000 fold decrease in short-circuit dark current is attributed to the elimination of primary butylamine ligands in the CQD film and their interaction with the Al contact. The noise associated with this electrochemical dark current previously limited the detectivity of CQD photodiodes to \(\sim 10^{10}\) Jones.

5.4.4 XPS Analysis of CQD Films

X-ray photoelectron spectroscopy (XPS) was used to examine the effect of BDT treatment and air annealing on the chemical composition of the PbS CQD films. The relative contributions of oxygen, sulfur, and lead species were measured in three films: a control film of CQDs with PBA ligands, a BDT treated film, and a BDT treated film with a subsequent anneal in an air atmosphere containing \(\text{H}_2\text{O}\). The species tracked, and their approximate energies are shown in Table 5.1.
Table 5.1. Oxygen, sulfur, and lead species tracked in the CQD films using XPS.

<table>
<thead>
<tr>
<th>Species</th>
<th>Energy [eV]</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O1s</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbOx</td>
<td>~529.2</td>
<td>lead oxide</td>
</tr>
<tr>
<td>Pb(OH)(_2)</td>
<td>~530.8 (74)</td>
<td>lead hydroxide</td>
</tr>
<tr>
<td>-COO(^-)</td>
<td>~532.2</td>
<td>carboxylate</td>
</tr>
<tr>
<td><strong>S2p</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbS</td>
<td>~160.7 &amp; ~161.9</td>
<td>lead sulfide (2:1 peak height ratio between energies)</td>
</tr>
<tr>
<td>S-C</td>
<td>~161.9</td>
<td>sulfur-carbon bond (in benzene dithiol)</td>
</tr>
<tr>
<td>poly-S(^2-)</td>
<td>~163.9</td>
<td>poly-sulfide (formed by BDT and excess BDT)</td>
</tr>
<tr>
<td>PbSO(_3)</td>
<td>~165.5</td>
<td>lead sulfite</td>
</tr>
<tr>
<td>PbSO(_4)</td>
<td>~167.8</td>
<td>lead sulfate</td>
</tr>
<tr>
<td><strong>Pb4f</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbS</td>
<td>~137.7</td>
<td>lead sulfide (CQD semiconductor core)</td>
</tr>
<tr>
<td>PbSO(_3)</td>
<td>~138.5</td>
<td>lead sulfite</td>
</tr>
<tr>
<td>PbSO(_4)</td>
<td>~138.5</td>
<td>lead sulfate</td>
</tr>
<tr>
<td>Pb(OH)(_2)</td>
<td>~138.5</td>
<td>lead hydroxide</td>
</tr>
<tr>
<td>PbCOO(^-)</td>
<td>~139.1 (77)</td>
<td>lead oleate (Pb bond to oleic acid ligand used in synthesis)</td>
</tr>
</tbody>
</table>
Figure 5.2. XPS spectra of O1s peaks (oxygen species). (a) Untreated CQD film. (b) BDT treated CQD film. (c) BDT treated and air annealed CQD film.
Figure 5.3. XPS spectra of S2p peaks (sulfur species). (a) Untreated CQD film. (b) BDT treated CQD film. (c) BDT treated and air annealed CQD film.
Figure 5.4. XPS spectra of Pb4f peaks (lead species). (a) Untreated CQD film. (b) BDT treated CQD film. (c) BDT treated and air annealed CQD film.
Figure 5.2 shows XPS spectra of O1s peaks (oxygen species). The untreated film shows well defined peaks for lead oxide, lead hydroxide, and carboxylate species. BDT dramatically reduces the magnitude (~10 fold) of all oxygen species peaks with only lead hydroxide remaining measurable after treatment. Air annealing restores the lead oxide and lead hydroxide peaks to magnitudes very similar those in the un-treated film.

Figure 5.3 shows XPS spectra of S2p peaks (sulfur species). The untreated film shows a well defined lead sulfide double-peak and a lead sulfite peak. The lead sulfide peaks are unaffected by BDT treatment. New peaks corresponding to the thiol sulfur-carbon bond and poly-sulfide species are present after BDT treatment and may obscure a lead sulfite peak. After the air anneal, the lead sulfide peaks remain unchanged, while the poly-sulfide peaks increase in magnitude.

Figure 5.4 shows XPS spectra of Pb4f peaks (lead species). The untreated film shows a well defined lead sulfide peak and a lead carboxylate peak corresponding to residual oleic acid ligand used in synthesis. A common peak for lead sulfite, lead sulfide, and lead hydroxide is also present. The lead sulfide peak is unaffected by BDT treatment. However, BDT treatment eliminates the carboxylate peak, indicating the displacement of remaining oleic acid with thiol ligands. After the air anneal, the lead sulfide peaks remain unchanged, while the common peak for lead sulfite, lead sulfide, and lead hydroxide is increased.
From the observations of the oxygen, sulfur, and lead species in the CQD film, it was concluded that the BDT treatment was highly effective in displacing oxygen species bonded to lead, resulting in a chemical reduction of the PbS CQDs. Annealing BDT treated films in an air atmosphere containing H$_2$O restores the oxygen species bonded to lead (lead oxide and lead hydroxide), resulting in a re-oxidization of the CQD film. The observed oxidation of a thiol treated lead chalcogenide CQD film by exposure to air is consistent with findings in a similar study using ethane thiol treated PbSe CQDs$^{74}$. An additional effect of the BDT treatment is the elimination of remaining oleic acid in the CQD film.

5.5 Photodiode Characterization

Fully optimized CQD photodiodes were characterized in terms of current-voltage, photoresponse efficiency, dark-current noise, and capacitance-voltage in order to develop a detailed physical understanding of device operation. The dependence of device characteristics and performance on temperature was also analyzed, yielding increased sensitivity as a result of the suppression of internal thermal noise.

5.5.1 Current-Voltage Characteristics

Figure 5.5 shows the steady-state current-voltage ($I$-$V$) characteristics of the CQD photodiode in the dark and at 17.9 $\mu$W.cm$^{-2}$ illumination at 1550 nm. The dark current characteristics are well described by a diffusion theory of emission over a potential barrier$^{59}$, as discussed in Section 4.4. The dark current density is 0.1 nA.cm$^{-2}$ at zero bias and 2.0 $\mu$A.cm$^{-2}$ at -1.0 V bias. Rectification of 120x was observed at +/- 0.5 V bias.
Under illumination, a photocurrent is generated in the direction opposite to the forward current of the diode, similar to conventional semiconductor diodes. The contribution of the photocurrent is most apparent at zero bias and reverse bias, as shown in Figure 5.5b. The photodiode also demonstrates modest photoconductivity, as indicated by the increase in forward bias current density under illumination shown in Figure 5.5a.

![Figure 5.5. Steady-state I-V characteristics in the dark and with 17.9 μW.cm⁻² illumination at 1550 nm on (a) linear and (b) log scales.](image)

### 5.5.2 Photoresponse and Sensitivity

Figure 5.6 shows external quantum efficiency (EQE) (at 295 K) and normalized detectivity (at 250 K) as a function of wavelength in the CQD photodiode. An EQE of 17% is achieved at 1450 nm and reaches a maximum of 52% at 580 nm. Photoresponse is measurable to 1800 nm, limited by the CQD absorption onset defined by quantum-size effect. D* is >10¹² Jones at 1450 nm for temperatures below 255K and >10¹² Jones at 1120 nm for temperatures below 280K.
The shape of the EQE spectrum follows the absorption spectrum of the CQD film, shown in Figure 5.7. The peak in the absorption and EQE at 1450 nm corresponds to the first CQD excitonic absorption feature while peaks in the absorption and EQE at shorter wavelengths are the result of Fabry-Perot interference in the thin CQD film.

Figure 5.6. External quantum efficiency (at 295 K) and normalized detectivity (at 250 K) as a function of wavelength.

Figure 5.7. Spectral absorption coefficient of the CQD film.
The dependence of the photoresponse on irradiance, bias, and illumination modulation frequency was measured. A common baseline was used for all measurements: zero bias and 17.9 μW.cm⁻² irradiance at 1450 nm at 100 Hz modulation.

The magnitude of the photocurrent is proportional to reverse bias, resulting in a dependence of photodiode EQE on bias, as shown in Figure 5.8a. Figure 5.8b shows photocurrent density as function of irradiance. The response is linear within 6% over 4 decades of irradiance.

![Figure 5.8](image)

Figure 5.8. (a) EQE as a function of reverse bias. (b) Photocurrent density as a function of irradiance.

The dramatic increase in EQE compared to previous CQD photodiode photodetectors was achieved by creating a large (0.20 V) built-in potential for photogenerated charge carrier separation. Controlled oxidization increased the doping of the CQD film (after treatment with a reducing agent, BDT) and the height of the Schottky barrier at the PbS
CQD/Al metallurgical junction. The optimal duration of the oxidation process was determined empirically to provide the largest built-in potential before growth of interfacial states at the metallurgical junction began to degrade EQE.

Figure 5.9 shows normalized photocurrent in the photodiode as a function of illumination modulation frequency. The 3 dB frequency is 10.7 kHz at zero bias and 1.95 μW.cm\(^{-2}\). The response is substantially flat up to the appearance of a pole at 1 kHz. A second pole appears at 50 kHz. Figures 2d and 2e show an exponential dependence of the 3dB frequency on irradiance and a sublinear dependence of the 3dB frequency on reverse bias. The maximum observed 3 dB frequency was 61.2 kHz at -1.0 V bias and 17.9 μW.cm\(^{-2}\) illumination.

Figure 5.9. Frequency response of the photocurrent at zero bias.
5.5.3 Temperature Dependence of Photodiode Performance

Photocurrent, current noise, and $I-V$ characteristics were measured as a function of temperature to investigate performance improvements with decreasing temperature and the dependence of the noise current on the shunt resistance-area product ($RoA$) of the CQD photodiode.

Figure 5.11a shows EQE at 1450 nm as a function of temperature. EQE increases with decreasing temperature as a result of decreased thermal carrier concentrations and decreased recombination rate at reduced temperatures.

Figure 5.11b shows $RoA$ as function of temperature: $1.5e5 \, \Omega \cdot \text{cm}^2$ at 295 increasing to $8.6e6 \, \Omega \cdot \text{cm}^2$ at 235 K. This value is comparable to highly optimized crystalline semiconductor photodiodes. $RoA$ increases with temperature due to decreased thermal emission of carriers over the Schottky barrier at the Al/PbS CQD junction.\(^\text{59}\)
Figure 5.11c shows measured $i_{\text{noise}}$ and the thermal current noise limit as a function of temperature. In the absence of illumination or applied bias, noise in photodiodes originates entirely from thermal noise,\textsuperscript{24,25} and can be calculated, based on the effective shunt resistance of the photodiode at zero bias ($R_o$) and the temperature. The measured current noise follows the thermal limit with decreasing temperature, but at magnitudes up to $\sim 2 \text{ fA.Hz}^{-0.5}$ greater. This excess noise may be attributed to a net dark current resulting from a small voltage overburden in the measurement equipment or environmental noise.

Figure 5.11d shows normalized detectivity ($D^*$) as a function of operating temperature. $D^*$ was calculated at 1450 nm, the first CQD excitonic feature, and 1120 nm, the wavelength of the CQD photocurrent response maximum. $D^*$ shows a linear dependence on temperature and is greater than $10^{12}$ Jones at 1120 nm for temperatures below 280K, and greater than $10^{12}$ Jones at 1450 nm for temperatures below 255K. Although measured using a cryostat, these temperatures are readily obtainable using low cost solid-state cooling.
Figure 5.11. (a) EQE at 1450 nm as a function of temperature. (b) Measured RoA as function of temperature. (c) Measured $i_{\text{noise}}$ and $i_{\text{noise}}$ calculated from measured RoA, as a function of temperature. (d) $D^*$ at 1450 nm and 1120 nm, as a function of temperature.

### 5.5.4 Depletion Width, Built-In Potential, and Fixed Charge Density

Measurements of capacitance as function of bias were used to determine built-in potential, fixed charge density, and depletion region width of the CQD film and junction. Figure 5.12a shows the fit of measured capacitance values to the depletion approximation\(^5\) (Section 4.4), revealing a built-in potential of 0.20 V, and a fixed charge (acceptor) density of $5.0 \times 10^{15}$ cm$^{-3}$. Figure 5.12b shows the depletion region width calculated from the measured capacitance, using a relative dielectric permittivity of 19.2,
and assuming a one-dimensional electric field distribution. The depletion width at zero bias is calculated to be 240 nm.

Figure 5.12. (a) Measured capacitance, as a function of bias, and best-fit using the abrupt junction approximation. (b) Depletion region width, as a function of bias, calculated from the measured capacitance.

### 5.5.5 Carrier Lifetime

Effective carrier lifetime in the CQD film can be calculated from the initial rate of the open circuit voltage decay (OCVD) of the CQD photodiode in response to cessation of illumination\(^78\). The open-circuit voltage \((V_{oc})\) represents the difference in energy of the electron and hole quasi-Fermi levels at the photodiode contacts. As the quasi-Fermi levels are directly dependent on the carrier concentrations, the rate of change of \(V_{oc}\) relates the rate of carrier population change. Assuming a simple model of recombination and low-level injection conditions,

\[
\frac{dn}{dt} = -\frac{n}{\tau},
\]

the carrier lifetime, \(\tau\), can be calculated from the initial rate of change of \(V_{oc}\),

\[93\]
\[
\tau = -\frac{k_b T}{q} \frac{1}{\frac{dV_{oc}}{dt}},
\]

(5.2)

where \(k_b\) is Boltzmann’s constant and \(T\) is the temperature. For materials with lifetimes dependent on irradiance, OCVD yields the carrier lifetime corresponding to the steady-state illumination level, as the \(V_{oc}\) transient is measured immediately following the cessation of illumination.

Figure 5.13a shows the initial open-circuit voltage decay transient in a CQD photodiode illuminated at 17.9 \(\mu\text{W.cm}^2\) at 1550 nm, following cessation of illumination at 0 ms. The linear fit to the initial decay rate is also shown. Figure 5.13b shows calculated carrier lifetimes for the range of irradiances used for photodiode characterization. Measured effective carrier lifetimes in the CQD film show a strong dependence on irradiance, ranging from tens of microseconds to hundreds of milliseconds over a range of irradiances from \(10^{-7}\) to \(10^{-3}\) W.cm\(^2\).

![Figure 5.13. (a) Open-circuit voltage transient decay and a linear fit to the initial decay rate. (b) Carrier lifetime as a function of irradiance at 1550 nm.](image)
Strong dependence of carrier lifetime on irradiance is observed in semiconductors with large trap densities\textsuperscript{79,80}. This effect is observed, typically at lower irradiances, when the concentration of excess carriers ($\Delta n$) is comparable to the concentration of carrier traps ($N_t$) in the material. At high irradiances, the dependence of carrier lifetime on irradiance saturates to a value representative of the recombination lifetime.

### 5.6 Model of Device Operation

We used measurements of the transient response to stepwise changes in illumination and the quantum efficiency as a function of irradiance to confirm and further elucidate the physical mechanisms underlying the operation of the CQD photodiode.

#### 5.6.1 Transient Photocurrent

Figure 5.14a shows the photocurrent response to a 500 $\mu$s square illumination pulse at photodiode biases of 0.0, -0.5, and -1.0V. At each bias, the transient response is composed of two distinct components – an initial, fast, linearly increasing component; and a slower, exponentially increasing component. The rise and fall characteristics of the photocurrent are symmetric. The fast photocurrent component is attributed to carriers generated in the depletion region ($G_{DR}$ in Figure 5.15) and quickly swept out by a drift current proportional to the built-in electric field ($E$). The total rise time of this component is equal to the depletion region transit time ($t_r = w_{DR}/(\mu_h E)$), where $\mu_h$ is the hole mobility, which is approximately the same for both electrons and holes, based on measured drift mobilities. The slower component is attributed to electrons generated in...
the quasi-neutral region ($G_{QNR}$ in Figure 5.15) which must diffuse to the depletion region. The rise time of this component is the time required for generation, diffusion, and recombination processes in the quasi-neutral region to reach a steady state, and is dependent on the width of the quasi-neutral region ($w_{QNR}$) and inversely dependent on the electron diffusion coefficient ($D_e$). The results of a numerical model used to test the capacity of this conceptual description to explain the photoresponse of the CQD photodiode are also shown in Figures 5.14a and 5.14b and are based on measured parameters of the CQD photodiode.

Figure 5.14. Photodiode transient response. (a) Measured (noisy line) and simulated (smooth line) photocurrent transient response as a function of bias to a 500 µs square illumination pulse at 17.9 µW.cm$^{-2}$. The measured and simulated lines are co-incident for 0.0V. (b) Measured and simulated photocurrent transient response (normalized) as a function of irradiance at zero bias. The simulated response is shifted for clarity.
Figure 5.15. Energy bands in the PbS CQD film near the Schottky barrier at the Al/PbS interface. Electrons and holes generated in the depletion region ($G_{DR}$) drift under the influence of the built-in electric field of the junction to the Al contact and the edge of the quasi-neutral region, respectively. Electrons generated in the quasi-neutral region ($G_{QNR}$) must diffuse to the edge of the depletion region where they are rapidly swept away by the built-in electric field. The movement of holes in the quasi-neutral region is governed by the relaxation of the p-type semiconductor.

5.6.2 Quantum Efficiency

Figure 5.16 shows measured and simulated CQD photodiode EQE as a function of irradiance. Photodiode EQE is independent of irradiance at irradiances $< 10^{-5}$ W.cm$^{-2}$, but begins to decrease at irradiances $> 10^{-5}$ W.cm$^{-2}$. This transition corresponds to the minimum carrier lifetime required for photocarriers generated in the quasi-neutral region to diffuse to the edge of the depletion region.
We propose that the external quantum efficiency of CQD photodiodes is ultimately determined by three processes, each characterized by an efficiency ranging from 0 to 1:

\[
\eta_{external} = \eta_{abs} \cdot \eta_{diss} \cdot \eta_{extr};
\]

\(\eta_{abs}\) is the fraction of the incident photon flux absorbed by the CQD film, \(\eta_{diss}\) represents the probability of photogenerated excitons dissociating into individual charge carriers, and \(\eta_{extr}\) quantifies the efficiency with which these charge carriers are transported, through drift and diffusion, to the contacts. Both \(\eta_{diss}\) and \(\eta_{extr}\) are dependent on traps in the CQD film which serve to prolong carrier lifetimes. \(\eta_{extr}\) is also dependent on the carrier transport time, which depends on the geometry and operating conditions of the photodiode. Further details of this model of CQD photodiode quantum efficiency are provided in Appendix B.

Absorbance efficiency is \(~37\%\) at the excitonic absorption feature (1450 nm) based on measured CQD film absorption and substrate and ITO contact transmittance. Extraction efficiency is expected to approach unity at irradiances up to \(10^{-5}\) W.cm\(^2\) given that the
drift length and diffusion lengths exceed the depletion region and quasi-neutral region depths, respectively (details provided in Appendix B). Dissociation efficiency must therefore lie in the range 39%-57%, depending on bias, to account for the observed external EQE of 17% to 25% at 1450 nm over the bias range 0.0 to -1.0 V. Thus, the quantum efficiency of the fully depleted QCD photodiode is limited by both the fraction of incident photons absorbed in the CQD film, and by the carrier dissociation efficiency.

5.6.3 Numerical Model

The photoresponse of the CQD photodiode is modeled based on measured carrier dynamics under zero-bias conditions. This approach isolates the photoresponse from the dark-current characteristics of the PbS CQD/Al Schottky barrier. For the irradiances considered, carriers are optically generated at low-levels compared to the equilibrium carrier concentration in the CQD photodiode. However, due to the strong dependence of measured carrier lifetime on irradiance, traditional low-level injection assumptions cannot be made. In the model, the measured carrier lifetime at each irradiance provides the dependence of carrier dynamics on free carrier and trap populations necessary to solve the continuity equations. This method provides a complete representation of the steady-state response of the photodiode and provides a good approximation to the transient response at each irradiance. The model can also be used to approximate the photoresponse at modest reverse bias, assuming that the concentration of electrically injected carriers is small compared to the concentration of optically injected carriers.
The CQD photodiode photoresponse is attributed to photogeneration of carriers in the depletion region (DR) and quasi-neutral region (QNR) of the CQD film\textsuperscript{59}. The width of the DR and the magnitude of the electric field within are a function of the CQD fixed charge density, the Schottky barrier characteristics, and the applied bias\textsuperscript{59}. The QNR and DR are treated separately, using the semiconductor continuity equations, with diffusion and drift dominating carrier transport in each region, respectively. Solutions of these equations are calculated using measured device and materials parameters (Table 8.1), allowing determination of the capacity of the model to explain the physics underlying operation of the CQD photodiode.

5.6.4 Numerical Model Implementation

A one dimensional representation of the photodiode is used, consistent with the planar architecture where both film thickness and carrier transport lengths are much smaller than the lateral dimensions. It is assumed that electric fields are normal to the plane of the device and any fringing fields at the device edges can be ignored. The abrupt depletion approximation is used to define a boundary between the QNR and DR, which are treated separately.

In the QNR there is no electric field and carriers are transported by diffusion. Holes are the majority carrier and are transported on a timescale on the order of the dielectric relaxation time, while minority carrier electron diffusion limits the rate of carrier transport. The continuity equation for excess electrons in the QNR is
\[
\frac{\partial \Delta n}{\partial t} = G - R + T + D_n \frac{\partial^2 \Delta n}{\partial x^2},
\]  

(5.3)

where \(\Delta n\) is the excess electron density, \(D_n\) is the electron diffusivity, \(T\) is the net rate of carrier trapping, and \(G\) and \(R\) are the generation and recombination rates, respectively.

The boundary conditions imposed on the QNR are \(d\Delta n/dx = 0\) at the ITO contact (no recombination), and \(\Delta n = 0\) at the edge of the DR (all carriers swept into the DR).

Within the DR, diffusion is assumed to be negligible and both electrons and holes drift in response to the electric field. Recombination in the DR is also assumed to be negligible as the drift transit time is much lower than measured carrier lifetimes. The continuity equation for excess holes in the DR is

\[
\frac{\partial \Delta p}{\partial t} = G + \Delta p \mu_p \frac{\partial E}{\partial x},
\]  

(5.4)

where \(\Delta p\) is the excess hole density, \(\mu_p\) is the hole mobility, \(G\) is the generation rate, and \(E\) is the average electric field in the DR. The average electric field is proportional to the built in potential of the junction, \(V_{bi}\), and the externally applied bias, assuming a portion of the externally applied bias is dropped across the Schottky barrier interface \((V_{int})^{59}\). The single boundary condition on the DR is \(\Delta p = 0\) at the Al contact (no electrical injection of carriers from the contact).

In both the QNR and DR, the generation rate is calculated based on an exponential decay of irradiance in the CQD film,

\[
G = T_{sub} \alpha \phi e^{-\alpha x} \eta_{diss},
\]  

(5.5)
where $T_{sub}$ is the net transmittance of the transparent substrate and ITO contact, $\alpha$ is the measured absorption coefficient of CQD film, $\phi$ is the incident photon flux, and $\eta_{diss}$ is the dissociation quantum efficiency of the charge carrier generation process (Supplementary Information 11). Reflection from the Al contact is also accounted for in the detailed implementation of the model.

Complete accounting of carrier populations in the CQD film includes both free carriers and carriers in traps

\begin{equation}
T = -\frac{n_t}{\tau_g} + \frac{\Delta n (1-n_t/N_t)}{\tau_t},
\end{equation}

where $\tau_g$ and $\tau_t$ are the trapping and escape times and $n_t$ and $N_t$ are the trapped carrier concentration and trap density, respectively. Under steady-state conditions, the trap population is constant ($T = 0$) and the density of free carriers remains identical to the value expected in the absence of carrier trapping.

Recombination is represented by a simple rate based on the effective carrier lifetime, $\tau_r$,

\begin{equation}
R = \frac{\Delta n}{\tau_r}.
\end{equation}

The effective carrier lifetime specifically represents steady-state illumination conditions rather than the transition between dark and illumination. However, the complete solution for excess carrier populations under steady-state conditions can be used as an approximate solution under transient conditions. Trap populations are expected to respond more slowly to changes in illumination than free carriers and, as an
approximation, can be represented as constant, allowing use of the simplified recombination term to estimate photodiode transient photoresponse.

The continuity equations are solved for $n$ and $p$ as a function of time and position using, a numerical partial differential equation solver. The total current in the CQD photodiode is continuous, as defined by the continuity equations; however, the photocurrent is limited by the least-expedient transport mechanism in each region of the device. The diffusion of minority carrier electrons limits the photoresponse of charge carriers generated in the QNR. The photocurrent density resulting from generation in the QNR ($J_{G,QNR}$) is calculated from the gradient of excess electrons in this region,

$$J_{G,QNR} = qD_n \frac{\partial \Delta n}{\partial x}. \quad (5.8)$$

Drift of majority carrier holes limits the photoresponse of charge carriers generated in the DR. The photocurrent density resulting from generation in the DR ($J_{G,DR}$) is calculated from the carrier density and the average electric field in the DR,

$$J_{G,DR} = q\Delta p \mu_p E. \quad (5.9)$$

The total photocurrent in the CQD photodiode is the sum of the components generated in the QNR and DR,

$$J = J_{G,QNR} + J_{G,DR}. \quad (5.10)$$

5.6.5 Summary of Measured Physical Parameters

Table 5.2 summarizes all measured CQD parameters and the values used in the numerical model to achieve good fits to the measured transient photocurrents.
Table 5.2. Measured physical parameters of the CQD photodiode.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Measurement Method</th>
<th>Measured Value</th>
<th>Value Used in Model</th>
</tr>
</thead>
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<tr>
<td>CQD Film Thickness [nm]</td>
<td>$d$</td>
<td>profilometer</td>
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<td>340</td>
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<tr>
<td>Depletion Region Thickness [nm]</td>
<td>$w_{DR}$</td>
<td>capacitance-voltage</td>
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<td>160 at $V_{bias} = 0.0$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>305</td>
<td>200 at $V_{bias} = -0.5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>320</td>
<td>220 at $V_{bias} = -1.0$</td>
</tr>
<tr>
<td>Quasi-Neutral Region Thickness [nm]</td>
<td>$w_{QNR}$</td>
<td>calculated from $d - w_{DR}$</td>
<td>100</td>
<td>180 at $V_{bias} = 0.0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>35</td>
<td>140 at $V_{bias} = -0.5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>120 at $V_{bias} = -1.0$</td>
</tr>
<tr>
<td>Built-in Potential [V]</td>
<td>$V_{bi}$</td>
<td>capacitance-voltage</td>
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<td>0.20</td>
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<td>Absorption Coefficient at 1550 nm [cm$^{-1}$]</td>
<td>$\alpha$</td>
<td>absorption</td>
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<td>5000</td>
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<tr>
<td>Substrate Transmittance at 1550 nm</td>
<td>$T_{sub}$</td>
<td>spectral transmission</td>
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<td>0.85</td>
</tr>
<tr>
<td>Dissociation Quantum Efficiency</td>
<td>$\eta_{diss}$</td>
<td>fit to measured photoresponse</td>
<td>0.39 at $V_{bias} = 0.0$</td>
<td>0.52 at $V_{bias} = -0.5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.57 at $V_{bias} = -1.0$</td>
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</tr>
<tr>
<td>Carrier Lifetime [s]</td>
<td>$\tau$</td>
<td>$V_{oc}$ transient</td>
<td>(Section 5.5.5)</td>
<td>(Section 5.5.5)</td>
</tr>
<tr>
<td>Relative Static Dielectric Permittivity</td>
<td>$\varepsilon_r$</td>
<td>CELIV</td>
<td>19.2</td>
<td>19.2</td>
</tr>
<tr>
<td>Hole Mobility [cm$^2$.V$^{-1}$.s$^{-1}$]</td>
<td>$\mu_h$</td>
<td>CELIV</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$1.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Electron Diffusivity [cm$^2$.s$^{-1}$]</td>
<td>$D_e$</td>
<td>calculated from time-of-flight and $\tau$</td>
<td>$3.8 \times 10^{-6}$</td>
<td>$1.9 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
5.6.6 Results

Using measured values for all physical parameters in the continuity equations, solutions for the excess electron and hole densities as a function of time and position were found, and used to calculate \( J_{G,QNR} \) and \( J_{G,DR} \). Figures 5.17a and 5.17b show the excess electron and hole concentrations in the quasi-neutral and depletion regions of the photodiode at equilibrium, at zero bias, under 17.9 \( \mu \text{W.cm}^{-2} \) illumination at 1550 nm. Under illumination, excess electrons accumulate in the QNR, limited by the carrier lifetime and the rate of electron diffusion to the edge of the DR. The hole concentration in the DR increases linearly with the distance from the CQD/Al interface, as recombination is negligible and all photogenerated carriers are swept out by the large built-in field.

![Figure 5.17](image)

Figure 5.17. Excess (a) electron and (b) hole concentration as a function of position in the CQD photodiode under steady-state illumination.
5.6.7 Interpretation of Photodiode Response Using Model Results

As shown in Figure 5.14a, with increasing reverse bias, both the measured and simulated responses show an increase in the magnitude of the fast photocurrent component and a decrease in the time required for the slow current component current to reach steady state. The magnitude of the fast component increases with reverse bias – a result of the increasing width of the depletion region ($w_{DR}$) with reverse bias (Section 5.5.4), and a commensurate increase in the number of photoca rriers generated in the depletion region. An increase in $w_{DR}$ results in a decrease of $w_{QNR}$ and a reduction in the time required to reach steady state in the quasi-neutral region. Both measured and simulated photocurrent show increasing response speed in the slow current component – a trend consistent with the observations of increasing 3dB frequency with increasing reverse bias, as shown in the Figure 5.10a.

Figure 5.14b shows a detailed view of the fast and slow photocurrent response to the onset of irradiances of 17.9, 107 and 492 $\mu$W.cm$^{-2}$. The current response is normalized to allow comparison of the transient response at each irradiance. Both measured and simulated results show an increase in the response speed of the slow current component with increasing irradiance, while the fast current component remains essentially unchanged. Decreasing carrier lifetime with increasing irradiance (Section 5.5.5) reduces the time required for the quasi-neutral region to reach steady state, thus increasing the response rate of the diffusive current component. This trend is consistent with the observations of increasing 3dB frequency with increasing illumination, as shown in Figure 5.10b.
These poles in the frequency response of the CQD photodiode shown in Figure 5.9 correspond to the time required to reach the steady state in the quasi-neutral region and the transit time of the depletion region, \( \sim 500 \mu s \) and \( \sim 10 \mu s \), respectively, as shown in Figures 5.14a and 5.14b.

## 5.7 Conclusions

The speed and sensitivity of the CQD photodiode represents a 3300 fold improvement in response speed and an 11 order-of-magnitude reduction in dark current density over the most sensitive CQD photodetector reported\(^1\). \( D^* \) values of \( 10^{12} \) Jones represent sensitivity on the order of commercially available photodetectors fabricated with crystalline semiconductors such as Si and InGaAs. Equally important, this represents a 100,000 fold improvement in sensitivity and response speeds up to 20% greater than the fastest CQD photodetector reported\(^2\).

The model of CQD photodiode operation, based on measured physical parameters and photocurrent response, provides insight into the mechanisms governing device operation. The contribution of drift and diffusion photocurrents from separate regions of the photodiode indicates the possibility for further device optimization if a means to control the photocurrent components can be established.
Chapter 6. Drift and Diffusion in CQD Films

6.1 Introduction

In CQD photodiodes, nearly equal proportions of charge carriers are predicted to be generated in the depletion region formed by the Schottky barrier and in the quasi-neutral region of the CQD film. Drift and diffusion both appear to be very effective mechanisms for transporting charge carriers out of the device and allowing their contribution to the photocurrent. However, the relative efficiencies of drift and diffusion are not well understood in CQD films.

Establishment of a quantitative understanding of the roles of drift and diffusion in the transport of photogenerated carriers requires detailed measurements of charge carrier mobility and diffusion length. Accurate knowledge of these parameters is prerequisite for implementing the CQD photodiode model.

Drift transport in CQD films is well established and has been reported in numerous studies of CQD films and devices. Initially, drift transport measurements were used to determine both mobility and diffusion length in CQD films. Carrier extraction by linearly increasing voltage (CELIV) and time-of-flight (TOF) were used to measure majority (hole) and minority (electron) mobilities, respectively, in PbS CQD films.
Minority carrier diffusion length was calculated from a mobility-lifetime product based on the TOF and open-circuit voltage decay measurements.

We found that minority carrier diffusion length limits photogenerated charge transport and the efficiency of CQD photodiodes. To ensure the accuracy of the minority carrier diffusion length measurements, and to address inconstancies in the mobility-lifetime product calculation, a direct measurement of minority carrier diffusion length was required.

Diffusive transport is not well-characterized and has not been investigated directly in CQD films. The steady-state photocarrier grating (SSPG) and spectral photocurrent measurement techniques allow direct measurement of the diffusion length of minority carriers semiconductors. Accurate measurement of diffusion length clarifies the contribution of carrier diffusion to the photoresponse and allows the architecture of CQD photodiodes to be optimized for maximum efficiency.

6.2 Charge Carrier Drift in CQD Films

6.2.1 Carrier Extraction by Linearly Increasing Voltage (CELIV)

Majority carrier hole drift mobility was measured directly in CQD photodiodes using the CELIV technique\textsuperscript{69}. Under rapid, linearly increasing reverse bias, the transient drift current of thermal equilibrium carriers extracted from the quasi-neutral region of a diode can be observed separately from the steady-state displacement current associated with the
diode junction capacitance. A geometric relationship, based on the thickness of the semiconductor film, allows determination of the drift mobility from the arrival time of the transient current maximum.

There are several advantages of this technique over more common time-of-flight (TOF) measurements. First, CELIV eliminates the requirement that the dielectric relaxation time of the semiconductor to be longer that the charge carrier transit time in the measurement. This requirement limits the application of TOF measurements to a subset of the CQD films used for photodiode applications. Direct measurement of mobility in photodiode devices using CELIV takes into account the effect of any device fabrication processes on the CQD film. Practically, measurement of mobility using CELIV also eliminates preparation of additional samples for measurement and any associated variation in materials and processing.

Figure 6.1. CELIV current transient showing the extracted equilibrium charge carrier component, Δj, and the steady-state displacement current component, j(0).
Figure 6.1 shows a typical CELIV transient current measured in a CQD photodiode. In this measurement, the reverse bias is linearly ramped from 0 V to 5 V in 10 μs. The current response shows two components: a small transient with amplitude $\Delta j$ corresponding to the extraction of equilibrium carriers and a larger steady-state displacement current with amplitude $j(0)$. The transient current reaches a maximum at $t_{max}$ after the bias ramp begins. For low conductivity materials, $\Delta j < j(0)$, and the majority carrier mobility, $\mu_h$, can be calculated from $t_{max}^{69}$,

$$\mu_h = \frac{2d^2}{3 \frac{dV}{dt} t_{max}^2 \left( 1 + 0.36 \frac{\Delta j}{j(0)} \right)},$$

where $d$ is the film thickness, and $dV/dt$ is the ramp rate of the reverse bias. This calculation takes into account a numerical correction factor for the extraction depth of the charge carriers$^{82}$. Measurements of BDT treated and air annealed PbS CQD photodiodes reveal a hole drift mobility ranging from $10^{-5}$ cm$^2$.V$^{-1}$.s$^{-1}$ to over $10^{-4}$ cm$^2$.V$^{-1}$.s$^{-1}$, with the highest mobilities observed in devices with the highest EQE and operating speed. Measurements of PbS CQD films prior to BDT treatment show a similar range of mobilities.

CELIV also provides a convenient measurement of the static dielectric permittivity of the CQD film. Based on assumed parallel plate geometry and full depletion of the CQD film, the static dielectric permittivity can be calculated from the displacement current. Measurements of BDT treated and air annealed CQD photodiodes reveal a relative static dielectric permittivity ranging from 17 to 21. The large value of the PbS CQD relative static dielectric permittivity is due, in part, to the very high value for bulk PbS (~165)$^{83,84}$. 
For semiconductors with low thermal equilibrium carrier concentrations, steady-state illumination of the semiconductor can be used to increase the steady-state carrier concentration\textsuperscript{69}. The carrier generation rate in the semiconductor should be uniform, but if it is not, this technique can be used to identify the polarity of the extracted carriers. Short wavelength illumination will generate more carriers closer to the illuminated surface of the semiconductor. Reduction of the time required to reach the transient current maximum indicates that the extracted carriers are generated closer to the illuminated contact of the device. For the case of the CQD photodiode, this corresponds to the ITO contact where holes are extracted under reverse bias. Thus confirming that CELIV is measuring the hole drift mobility – the majority carrier in p-type PbS CQDs.

6.2.2 Time-of-Flight (TOF)

Minority carrier electron drift mobility was measured in specially prepared photodiodes with very thick (800 nm) CQD films using the time-of-flight technique. Pulsed laser illumination incident on the ITO contact creates electron hole pairs which are extracted at the Al and ITO contacts, respectively, analogous to previously described photodiode operation. However, by using short wavelength illumination (527 nm), corresponding to an absorption depth of \~200 nm, carrier generation occurs in a small volume of the CQD film adjacent to the ITO contact. By applying a large reverse bias (up to -10V), photogenerated electrons are swept across approximately the whole length of the fully depleted CQD film before being extracted at the Al contact. The transit time of the electrons, $t_{tr}$, can be measured, and the electron mobility, $\mu_e$, calculated,
\[ \mu_e = \frac{d^2}{V t_{tr}}, \]

where \( d \) is the film thickness and \( V \) is the applied bias. Carrier transport in CQD films is dispersive, resulting in the appearance of an inflection point in the log-log plot of the TOF photocurrent transient corresponding to the transit time \(^{85}\), as shown in Figure 6.2a. An electron mobility of \( 1.5 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \) was calculated from the linear dependence of \( 1/t_{tr} \) on the electric field in the CQD film, as shown in Figure 6.2b. Measured transit times at electric fields of \( 5 \times 10^{-4} \text{ V} \cdot \text{cm}^{-1} \) and lower were limited by the relaxation time of the CQD film and were not included in the calculation of drift mobility.

![Figure 6.2](image)

Figure 6.2. (a) TOF photocurrent transient at an electric field of \( 8 \times 10^4 \text{ V} \cdot \text{cm}^{-1} \) demonstrating an inflection point at 6 \( \mu \text{s} \). (b) \( 1/t_{tr} \) as a function of electric field.

The extracted photocharge is much smaller than the capacitive charge of the photodiode, indicating that the electric field within the diode could be considered constant during photocarrier extraction. The RC timeconstant of the photodiode and resistive load, and
the duration of the illumination pulse were ~50 ns and 150 ns, respectively; much shorter than the timescales of interest in the TOF measurement.

6.2.3 Drift Transport in CQD Photodiodes

Charge carrier drift occurs predominantly in the depletion region of CQD photodiodes, as this is the only region with a significant electric field. For a nominal device with a depletion region width of ~100 nm, a hole mobility of ~5x10^{-4} \text{ cm}^2.\text{V}^{-1}.\text{s}^{-1}, and a built-in potential of 0.2 V, transport across the depletion region takes only 1 \mu s, while the hole drift length, limited by a carrier lifetime of 10 \mu s, is 1 \mu m. These calculations indicate that drift transport will not limit the photogenerated charge collection efficiency of a CQD photodiode unless the depletion region is increased in width by ~10 fold, or mobility or electric field is reduced by a similar factor.

6.3 Charge Carrier Diffusion in CQD Films

6.3.1 Mobility Lifetime Product

To date, there have been no direct measurements of carrier diffusivity and diffusion length in CQD films. Instead, diffusion length is estimated based on measured minority carrier mobility and lifetime. Assuming that Einstein’s relation holds in semiconductor materials exhibiting dispersive transport\textsuperscript{86}, the diffusivity of free electrons can be calculated from the measured electron drift mobility,

\[
D_e = \frac{k_b T}{q} \mu_e, \tag{6.3}
\]
yielding an electron diffusivity of $3.8 \times 10^{-6} \text{ cm}^2.\text{s}^{-1}$. This value represents an upper limit on minority carrier electron diffusivity, as the TOF measurement takes into account only the effects of shallow traps on carrier mobility.$^{87}$.

Using carrier lifetimes measured using OCVD (Section 5.5.5), the diffusion equation yields diffusion lengths ranging from 230 nm to over 1 $\mu$m. The prediction of diffusion lengths greater than ~300 nm is not consistent with the observation of decreased quantum efficiency in CQD photodiodes with films substantially thicker than ~400 nm. This discrepancy is likely attributable to the sensitivity of the OCVD measurement to minority carrier trapping in the CQD film.

### 6.3.2 Steady-State Photocarrier Grating (SSPG)

Direct measurement of charge carrier diffusion length, $L_{\text{diff}}$, in CQD films was initially attempted using the steady-state photocarrier grating (SSPG) technique.$^{88,89}$ SSPG measurements record the steady-state photoconductivity of a semiconductor as a function of the period of an illumination interference pattern (grating) generated on the surface of the semiconductor by two coherent light sources. Under low electric fields, photoconductivity is independent of the period of the grating for periods less than the minority charge carrier diffusion length. When the period is increased beyond the diffusion length, conductivity will decrease, as minority carriers are unable to diffuse between the nodes of the grating. This change in conductivity is due solely to the microscopic charge carrier distribution – the average irradiance of the semiconductor and the average carrier generation rate are unchanged as the period of the grating is increased.
The minority charge carrier $L_{\text{diff}}$ is calculated from the ratio of the photocurrent with the grating (produced by two coherent sources) and without the grating (produced by the same sources, but incoherently), as a function of the grating period,

$$\beta = \frac{I_{\text{coherent}}}{I_{\text{incoherent}}}. \quad (6.4)$$

Based on a solution to the continuity equation for a spatially varying charge carrier generation rate, a relationship between $\beta$ and $L_{\text{diff}}$ is derived\textsuperscript{88,89},

$$L_{\text{diff}} = \frac{\Lambda}{2\pi} \sqrt{\phi} \sqrt{\frac{2}{1 - \beta^2}}, \quad (6.5)$$

where $\Lambda$ is the grating period and $\phi$ is a fitting parameter representing the quality of the grating. Figure 6.3 shows $\beta$ as a function of grating period for a CQD film and the corresponding fit to Equation (6.5) yielding a 65 nm diffusion length. A +/- 5 nm confidence interval to the fit is indicated by the dashed lines.

Figure 6.3. SSPG $\beta$ as a function of grating period yielding $L_{\text{diff}} = 60$ nm.
However, good fits between measured values of $\beta$ and the theoretical relationship between $\beta$ and $L_{\text{diff}}$ were only achieved at high illumination intensities with very slow illumination modulation frequencies (2 Hz). (Illumination modulation and lock-in techniques were required to resolve the small changes in photocurrent resulting from the grating.) These limitations were attributed to the strong dependence of the measurement on minority carrier electron trapping in the CQD film. As a result, SSPG appeared to have only limited use in measuring diffusion lengths in CQD films intended for photodiode applications. A diffusion length measurement technique that avoided trap-dominated photoconductive measurements was required.

### 6.4 Diffusion Length Measurement with Photocurrent Spectroscopy

#### 6.4.1 Introduction

In this report, we present direct measurements of minority carrier diffusion length in CQD photodiodes using photocurrent spectroscopy. Spectral measurements offer spatially controlled excitation with resolution on the order of nanometers without electron beam or other highly focused excitation sources. Photocurrent measurement directly examines collected charge carrier quantities without the need to establish a relationship between carrier populations and quasi-Fermi level locations, as required for open circuit voltage measurements such as surface photovoltage. Photocurrent is also linear over a much greater range of irradiance than open circuit voltage, allowing more accurate determination of diffusion length at higher irradiances$^{90}$. Furthermore, measurement of
$L_{\text{diff}}$ in finished CQD photodiodes takes into account any effects on carrier lifetime and diffusion length resulting from formation of the diode junction\textsuperscript{91}. Short-circuit photocurrent measurement has been used previously to measure $L_{\text{diff}}$ in crystalline and organic semiconductors\textsuperscript{92-94}. Measurements of $L_{\text{diff}}$ in silicon photodiodes have shown to yield diffusion lengths essentially equal to those derived using the widely-employed surface photovoltage technique\textsuperscript{90}. Spectral photocurrent measurements of the exciton diffusion length in organic semiconductors reveal length scales on the order of 250 nm – similar to length scales of minority carrier diffusion predicted in CQD films.

### 6.4.2 Isolating the Photocurrent Diffusion Component

CQD photodiodes were prepared using CQD synthesis, processing, and film deposition methods identical to those described in Chapter 5. Contacts, however, were deposited differently in order to reduce the depletion region associated with the Schottky barrier.
Figure 6.4. (a) Schematic, cross-sectional representation of the CQD Schottky barrier diode architecture. (b) Energy bands in the PbS CQD film near the Schottky barrier at the Al/PbS interface. Electrons generated in the quasi-neutral region ($G_{QNR}$) must diffuse to the edge of the Al/PbS interface where they are rapidly swept into the Al contact.

To isolate the diffusive component of the photocurrent, CQD photodiodes were fabricated with very narrow depletion regions, such that the measured photocurrent was generated nearly exclusively in the bulk of the CQD film. This was accomplished through the use of a two-component Schottky contact consisting of a very thin (~5 nm) Al layer at the CQD surface followed by a 40 nm ITO layer for electrical continuity. Thinning the Al layer reduced the effective work function difference between the metal contact and the CQD film$^{95,96}$, resulting in a reduction of the built-in-potential and exposed charge volume at the Schottky barrier. Reducing the depletion width through Schottky contact tuning allowed measurement of $L_{diff}$ in CQD films identical to those used in CQD photodiodes with full Schottky barriers.
Figure 6.5 shows the transient photocurrent response of CQD photodiodes with full and reduced Schottky barriers. The complete Schottky barrier photodiodes demonstrate a photocurrent response composed of two components: a fast, linearly rising component proportional to the depletion region width and applied bias, and a slower, exponential component with a time constant that depends on the incident irradiance. The fast component is attributed to photocarriers generated in the depletion region of the CQD film while the slow component results from photocarriers generated in the quasi-neutral region of the film. The photodiode with the reduced Schottky barrier and depletion region width shows only the slower diffusive component. The time constant of the slower component of the transient photocurrent response is insensitive to both built-in potential and applied bias, indicating a transport process independent of any electric field in the CQD film.

Further evidence for the suppression of the depletion region in the reduced Schottky barrier devices is evidenced in capacitance-voltage characteristics that fail to show the characteristic dependence of capacitance on bias observed in CQD photodiodes with well-defined depletion regions\textsuperscript{59}. 
Figure 6.5. Photocurrent transient response to a 500 μs square illumination pulse (17.9 μW.cm⁻² at 1550 nm). The response of the reduced Schottky barrier device is shifted in time by 100 μs for clarity.

### 6.4.3 Spectral Absorption Coefficient Measurement

The spectral absorption coefficient was measured using five identically processed CQD films with thickness ranging from 490 to 820 nm using a calibrated spectrophotometer in transmission mode. Fabry Perot interference in these relatively thick films was minimal over the wavelength range analyzed. The spectral absorption coefficient and the net absorption in the films were calculated from the exponential dependence of absorption on film thickness. This allowed isolation of film absorption while avoiding measurements or assumptions of optical coupling efficiency between the CQD films, the transparent substrates, and the air interface on the other side of the film. Figure 6.6 shows the measured spectral dependence of the absorption coefficient. The roll-off of the absorption coefficient at low wavelengths in two of the samples corresponds to the
thickest films measured (~800 nm). In these films, absorption is nearly 100% at shorter wavelengths, resulting in a greater uncertainty in measured transmittance values.

![Graph showing absorption coefficient vs. wavelength]

Figure 6.6. Measured spectral dependence of the absorption coefficient in 5 CQD films.

### 6.4.4 Photocurrent Spectroscopy Measurements

Two sets of CQD photodiodes were fabricated with two difference CQD batches. Each set consisted of between 1 and 4 identical devices patterned on the same CQD film. All CQD films and devices were processed identically. For each device, photoresponse was measured over the spectral range of 500 to 900 nm. This range was selected to provide a nearly linear, monotonically increasing absorption coefficient with decreasing wavelength. All measurements were performed at zero bias, at room temperature, in air, at 1000 Hz illumination modulation. A 940 nm CW illumination source was used to ensure uniform CQD film conductivity as the excitation wavelength was varied.
6.4.5 Model

Determination of materials parameters from a measured device photoresponse requires a model of the CQD photodiode that is consistent with the physics underlying device operation. The photocurrent response model introduced in Section 5.6 was used, with appropriate modifications to eliminate the depletion region. The model uses measured values of all CQD photodiode parameters, including the effective carrier lifetime, $\tau$, determined from the photocurrent transient response. Minority carrier diffusivity, $D_n$, is the sole fitting parameter; determined from the best fit to the measured photocurrent. Diffusion length is then calculated from $L_{diff} = \sqrt{\tau D_n}$.

The detailed numerical model of the CQD photodiode eliminates the need for the simplifying assumptions used to derive analytic solutions to the continuity equation\textsuperscript{90}. While analytically derived expressions for photoresponse provide compact representations and simple relationships between parameters, the constraints imposed by the simplifications preclude their application to materials which do not meet specific relationships between parameters such as the absorption coefficient and $L_{diff}$. Complete solutions also take into account subtleties of device operation, such as differences in recombination rate as a function of position, and may reduce sensitivity to errors in measured parameters\textsuperscript{97}. 
6.4.6 Results and Discussion

Figure 6.7 show the spectral photocurrent response for the two CQD devices. The photoresponse varies strongly with wavelength due to the variation of the absorption coefficient with wavelength, as shown in Figure 6.6. At shorter wavelengths, illumination is strongly absorbed at the incident side of the CQD film, far from the Schottky barrier where photogenerated electrons are collected. For longer wavelengths, absorption is weaker, and more photons reach the region of the CQD film near the Schottky barrier where they can be absorbed and the photogenerated carriers efficiently collected.

The fit of the numerical model is included in Figure 6.6 for each device. Variation of total photocurrent with excitation wavelength shows good agreement between measurements and model, allowing extraction of $L_{diff}$ of 12 nm, 60 nm, and 115 nm for devices 1 and 2, and device 2 after 36 days of ambient exposure, respectively. These values are consistent with average measured external quantum efficiencies of 0.4%, 4.2%, and 7.4% at 1550 nm.

The range of values for $L_{diff}$ is in good agreement with the value of 65 nm obtained using SSPG. The SSPG technique compliments the spectral photocurrent technique by eliminating the dependence on spectral absorption variation, the photodiode model, and its assumptions on the mechanisms of carrier transport in the photodiode.
Figure 6.7. Measured spectral photocurrent and fits to the photocurrent for devices demonstrating 115 nm, 60 nm, and 12 nm diffusion lengths. A confidence interval of +/- 2 nm and +/- 5 nm is shown for devices 1 and 2, respectively.

6.5 Diffusion Length Increase with Exposure to Ambient

To elucidate the origins of the significant increase in $L_{\text{diff}}$ observed in CQD photodiodes after exposure to ambient conditions, the effective lifetime of untrapped carriers in CQD films was analyzed, as a function of film treatment and ambient exposure, using quasi-steady-state photoluminescence (PL).

6.5.1 Photoluminescence

PL Theory

PL is a fast, non-contact, non-destructive and well-established characterization method for evaluation of defects in semiconductor materials. Photoluminescent intensity, $I_{\text{PL}}$, represents the rate of radiative recombination in a semiconductor, $R_{\text{rad}}$, and is
proportional to the excess, untrapped carrier concentration, $\Delta n$, resulting from illumination. The relationship between PL and untrapped carrier lifetime is governed by the continuity equation. Under equilibrium, in a semiconductor with no current flow, the generation rates, $G$, and recombination rates, $R$, of excess carriers are equal. The dominant recombination mechanisms in typical semiconductors are radiative, Auger, and Shockley Read Hall. Thus,

$$G_{opt} = R_{rad} + R_{Aug} + R_{SRH}$$  \hspace{1cm} (6.6)

$$G_{opt} = \frac{\Delta n}{\tau_{rad}} + \frac{\Delta n^2}{\tau_{Aug}} + \frac{\Delta n}{\tau_{SRH}}$$,  \hspace{1cm} (6.7)

assuming low-level injection conditions ($\Delta p = \Delta n \ll p_o$). Radiative and Auger recombination lifetimes, $\tau_{rad}$ and $\tau_{Aug}$, are determined by fundamental characteristics of the semiconductor. The SRH lifetime, $\tau_{SRH}$, depends strongly on the presence of recombination centres, which are typically associated with defects and impurities in the semiconductor.

For a constant value for $G_{opt}$, variation in measured $I_{PL}$ is inversely proportional to $\tau_{SRH}$. This dependence allows relative changes in $\tau_{SRH}$ to be monitored as a function of material processing. Under low-level injection conditions, the rate of Auger recombination is small compared to radiative and SRH recombination and can be assumed to be negligible. Based on this simplification, a direct relationship is observed between $I_{PL}$ and changes in non-radiative carrier lifetime:

$$I_{PL} \sim \frac{\Delta n}{\tau_{rad}} = G_{opt} - \frac{\Delta n}{\tau_{SRH}}.$$  \hspace{1cm} (6.8)
The effective lifetime of untrapped excess charge carriers, $\tau_{\text{eff,untrapped}}$, is the inverse sum of the reciprocal lifetimes associated with each of the recombination mechanisms,

$$\frac{1}{\tau_{\text{eff,untrapped}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{Aug}}} + \frac{1}{\tau_{\text{SRH}}}.$$  \hspace{1cm} (6.9)

Assuming low-level conditions and a short SRH lifetime, the untrapped effective carrier lifetime is determined primarily by the non-radiative recombination lifetime. Based on these relationships, relative changes in $I_{\text{PL}}$ is used to infer relative changes in $\tau_{\text{eff,untrapped}}$,

$$I_{\text{PL}} \sim G_{\text{opt}} - \frac{\Delta n}{\tau_{\text{eff,untrapped}}}.$$  \hspace{1cm} (6.10)

A quantitative relationship between these parameters can be established if $I_{\text{PL}}$ is known exactly, however this is difficult in practice. A method for determining $\tau_{\text{eff,untrapped}}$ from relative $I_{\text{PL}}$ measurements has been proposed, but relies on a numerical fitting parameter to establish the relationship between $I_{\text{PL}}$ and $\Delta n$.

Under steady state conditions, the untrapped excess carrier concentration, $\Delta n$, is independent of the density and occupancy of traps in the semiconductor. Steady-state PL measurements allow the untrapped lifetime to be measured independent of the effect of minority carrier traps that can significantly influence measurements such as OCVD.

**PL in CQDs**

The photoluminescence of CQDs is limited by surface irregularities that act as non-radiative recombination pathways for charge carriers. Photoluminescence quantum yield represents the ratio of photons emitted radiatively to photons absorbed in a material. PL quantum yields approaching unity in solution indicate the effectiveness of organic
ligands for passivating non-radiative recombination centres on the surfaces of lead chalcogenide CQDs. Substantially lower PL quantum yields are typically observed in CQD films. In films, carrier transport between dots becomes much more probable and non-radiative recombination centres can affect carrier populations in more than one CQD.

**Correlation between PL intensity and L\text{diff}**

Diffusion length in a semiconductor is proportional to the square root of carrier lifetime, \(\tau\), and the diffusivity, \(D\);

\[
L_{\text{diff}} = \sqrt{D\tau}.
\] (6.11)

Increases in diffusion length are expected to be proportional to increases in effective carrier lifetime. However, the quantitative dependence of \(\tau\) on the trapped and untrapped carrier lifetimes in CQD films is not yet established and prevents strong conclusions to be drawn from measurements of relative changes in untrapped excess carrier lifetime.

Several studies report a qualitative relationship between measured \(I_{PL}\) and \(L_{\text{diff}}\) in both crystalline and polycrystalline semiconductor materials. Spatial variation of \(I_{PL}\) and \(L_{\text{diff}}\), measured with surface photovoltage, were well-correlated in 2D mapping of Si and InGaAs wafers\textsuperscript{101}, and in polycrystalline Si wafers\textsuperscript{102}. The correlation between \(I_{PL}\) and \(L_{\text{diff}}\), measured with electron beam induced current, was also observed in CdZnTe single crystals\textsuperscript{103}. A recent study developed a quantitative relationship between these parameters in order to predict \(L_{\text{diff}}\) from measured \(I_{PL}\) resulting from front-side and back-side illumination of a semiconductor with a known absorption coefficient\textsuperscript{104}. However,
no comparison of the calculated $L_{\text{diff}}$ with an established diffusion length measurement technique was provided.

### 6.5.2 Measurement of PL in CQD Films

Samples for PL measurement were prepared by depositing CQD films on glass substrates without electrical contacts. The details of the PL measurement technique are provided in Appendix A.2.9. The laser excitation source for the PL measurements provides approximately uniform illumination of the CQD film. No electrical fields or significant potential gradients exist in the CQD films and no significant transport of equilibrium or photogenerated carriers is expected.

Combined with XPS analysis of isolated CQD films (Section 5.4.4), these techniques isolate the physical properties of the CQD film from those of the Schottky barrier structure, allowing direct analysis of changes in the CQD film as a function of chemical treatments and exposure to ambient conditions.

### 6.5.3 Results

**PL as a Function of BDT Treatment and Ambient Exposure**

PL was measured in four identically processed CQD films as a function of treatment and ambient exposure time. Films were measured as-deposited with PBA ligands, immediately after BDT ligand exchange, and at intervals during exposure to an ambient
atmosphere. The progression of a representative measured PL emission spectrum is shown in Figure 6.8.

![Graph showing PL emission spectrum evolution](image)

**Figure 6.8.** Evolution of the PL emission spectrum as a function of CQD film treatment and exposure to an ambient atmosphere. The absorption spectrum measured at the end of the aging experiment is also shown, with an arbitrary magnitude scaled to the PL spectra.

A single, well-defined photoluminescence emission peak was observed at wavelengths ranging from 1300 to 1700 nm. The width of the PL peak is equivalent to that of the first excitonic absorption peak. In all films, the magnitude of the PL emission increases after BDT treatment, and increases further with exposure to ambient conditions. Any radiative emission from states within the bandgap may not be captured due to the limited range of spectrometer in the IR.

The PL peak is initially centered at 1590 nm for the CQDs in solution, the as-deposited CQD film, and the BDT treated film. The peak shifts ~80 nm toward shorter wavelengths
upon exposure to an ambient atmosphere, and remains centered at 1510 nm through ongoing exposure. Although apparent in Figure 6.7, it is difficult to ascertain if broadening of the emission spectra is occurring during ambient exposure. The width of the PL peak prior to aging may be partially obscured by the spectrometer cutoff at 1700 nm or the measurement noise floor.

As shown in Figure 6.9, the first excitonic absorption peak is initially centered at 1450 nm in solution. Red shifts of 15 nm and 55 nm are observed after film formation and BDT treatment, and correspond to delocalization of electronic states as CQDs become close-packed\textsuperscript{5,105}. Exposure to ambient conditions for 8 days results in a \textasciitilde130 nm shift of the absorption peak toward shorter wavelengths.

![Figure 6.9. Normalized spectral absorption as a function of CQD film treatment and exposure to ambient conditions.](image-url)
A Stokes shift of ~120 nm was measured in PbS CQDs in solution and in as-deposited films. This shift was reduced ~2 fold after BDT treatment, and returned to the original value after exposure of CQD films to ambient conditions. The magnitude of the Stokes shift corresponds to 9% of the total bandgap energy and 17% of the quantum confinement energy.

**PL as a Function of Vacuum Exposure**

After exposure to ambient conditions for 8 days, CQD films were placed under vacuum to determine the role of weakly adsorbed species on untrapped excess carrier lifetime. PL was measured with the sample in an evacuated cryostat. Pumping at 10 mTorr for 2 hours increased PL emission by 20% to 40%. Further pumping for up to 18 hours showed a slight decrease in PL emission. A small (20 nm) red shift of the PL peak accompanied the increase in PL emission. After vacuum pumping, re-exposure to ambient conditions rapidly returned PL emission to previous levels.
Figure 6.10. PL as a function of CQD film exposure to vacuum after ambient exposure.

XPS

The XPS measurements presented in Section 5.4.4 monitored CQD film composition as a function of BDT treatment and ambient exposure. BDT treatment results in elimination of carboxylate species present in the as-deposited PBA passivated CQDs. Throughout the BDT exchange and subsequent ambient exposure, an increase in PbSO$_3$ and PbSO$_4$ species was observed.

6.3.4 Discussion

Stokes Shift and Near-Band-Edge emission

The single PL emission wavelength and relatively small Stokes shift suggest PL is attributable to near-band-edge recombination in the CQD film. The heterostructure interface at the CQD surface is prone to irregularities such as crystal lattice defects,
dangling bonds, oxidation, or adsorbed impurities that act as traps and recombination centres\textsuperscript{106-108}. The distribution of these localized states extends slightly into the energy bandgap of the semiconductor\textsuperscript{109}. In addition to forming non-radiative recombination centres, some of these states dominate radiative recombination in the CQDs, resulting in reduced luminescent photon energies as carriers recombine at states within the bandgap\textsuperscript{110-113}. The relative invariance of the Stokes shift during CQD film formation and subsequent oxidization indicates the stability of the energy distribution of the radiative recombination centres.

**PL and Absorption Peak Shift and Oxidation**

Blue shift of the PL emission and the first excitonic absorption peak after ambient exposure of the CQD films is consistent with oxidation of the CQD surfaces resulting in a net decrease in CQD size\textsuperscript{112,114} and an increase of the effective bandgap, as determined by size quantization. The spectral bandwidth of the PL emission is roughly comparable to the bandwidth of the first excitonic absorption peak of the CQDs, indicating that inhomogeneous broadening (particle size, shape, and defect distribution\textsuperscript{106}) in the CQDs dominates the feature width of the absorption and emission spectra.

**PL Intensity Increase with CQD Oxidation**

A five-fold increase in relative PL intensity is observed over 8 days of exposure of the PbS CQD film to ambient conditions. Over this same time, the PL emission peak shifted \~90 nm toward the blue. Increasing PL with ambient exposure has also been observed in
PbTe CQDs\textsuperscript{114} and PbS nanoparticles\textsuperscript{115}, indicating that oxidation of lead chalcogenides may lead to improved surface passivation.

The formation of native oxides or metal-deficient layers on the surface of bulk lead chalcogenide crystals serves to passivate the material and reduce the rate of further oxidation \textsuperscript{116,117}. Similar mechanisms may also be at work at the surfaces of the CQDs, where an increase in sulfite and sulfate concentrations were observed after BDT treatment and after ambient exposure. XPS measurements also showed that lead hydroxide and lead oxide species returned to pre-BDT treatment concentrations after ambient exposure. PbS nanoparticles purposely fabricated with a lead hydroxide surface passivation were observed to have significantly higher PL emission than similar particles without passivation\textsuperscript{115}.

XPS showed the displacement of carboxylate at the CQD surface after the BDT treatment. Carboxylate was identified to be a source of deep, long-lived electron traps in PbS CQD films passivated with primary butylamine\textsuperscript{77}. Elimination of deep traps/recombination centres is consistent with the observation of increased untrapped excess carrier lifetime and diffusion length following ambient exposure.

Increasing PL emission intensity with oxidation is not universally observed in CQD films. Deterioration of PL emission intensity in PbTe CQDs films was observed over the course of ambient exposure for several weeks\textsuperscript{114}. Similar observations have also been made in cadmium chalcogenide films\textsuperscript{112}. Deterioration of cadmium chalcogenides with
oxidation is attributed to the formation of volatile oxide species which subsequently evaporate, leading to continued erosion of the material\textsuperscript{106}. However, there are also reports of increased PL with certain types of oxidation of CdSe CQDs, where one type of oxidation enhances PL while the other quenches PL\textsuperscript{110}. The differences in response of lead and cadmium chalcogenide CQDs to ambient exposure may be due to differences in surface chemistry\textsuperscript{114} and the presence of additional adsorbed species.

**Adsorbed Species**

Vacuum treatment increased PL emission intensity, indicating that adsorbed species quench PL by providing sites for non-radiative recombination. Control over the trap spectrum in dielectrics such as lead sulfates is possible through adsorption of molecules from gaseous phase due to coordination of defects\textsuperscript{118}. However, the role of adsorbed species in CQD PL emission efficiency is unclear. There are conflicting studies reporting both enhancement and quenching of PL upon exposure of lead and cadmium chalcogenide CQDs to oxygen\textsuperscript{113,114,119,120}, air\textsuperscript{110,113,120}, and water\textsuperscript{108,112,115}. These contradictory reports indicate that NC synthesis and treatment determine the surface passivation properties and the associated sensitivity to external agents\textsuperscript{114}. A detailed analysis of the effects of these gasses on PbS CQDS is needed to determine the particular species responsible for the PL enhancement under vacuum.

### 6.3.5 Summary and Consistency with Device Performance

Increased untrapped carrier lifetime is attributed to the growth of native oxide species at the surface of the CQDs that act to suppress non-radiative recombination centres.
Increased untrapped carrier lifetime is consistent with the observation of increased charge carrier diffusion length and improved diffusive transport efficiency. However, it cannot be concluded that the increase in diffusion length is a consequence of increased untrapped carrier lifetime alone.

In photodiodes, increased $L_{\text{diff}}$ leads to an increased photogenerated carrier collection volume and increased photovoltaic device quantum efficiency. Increased overall device efficiency as a result of ambient annealing is consistent with observations in other lead chalcogenide semiconductor nanocrystal photovoltaic devices. As $L_{\text{diff}}$ varies significantly between films, it may be possible to further increase the efficiency of CQD photodiodes through maximization of carrier collection based on diffusive transport. The observation of oxidation in the CQD film further supports the assumption that the photoresponse of the reduced-barrier CQD photodiode is dominated by diffusive transport. Oxidation of PbS leads to the formation of minority carrier traps that act as electron acceptors, effectively doping the film p-type. An increase in the proportion of oxidation therefore leads to an increased effective dopant concentration and a decrease in the width of any depletion regions. If carrier transport was dominated by drift, this would result in a decrease in photocurrent, as the carrier collection volume is reduced. In fact, the opposite is observed – an increase in photocurrent with increased oxidation.

### 6.4 Conclusions

Majority carrier mobilities in PbS CQD films with ligands exchanged to primary butylamine demonstrated mobilities ranging from $10^{-5}$ to over $10^{-4}$ cm.V$^{-1}$.s$^{-1}$. These
mobilities are essentially unaffected by solid-state treatment of the CQD films with benzene dithiol and subsequent controlled oxidation. The EQE of CQD photodiodes is not limited by the majority carrier mobility. Transport times in the depletion region are far lower than the carrier lifetime and recombination in the depletion region is minimal. Spectral photocurrent measurements provide direct measurement of minority carrier diffusion length in CQD photodiodes. Measured diffusion lengths of 12 nm, 60 nm, and 115 nm provide good explanation of the measured external quantum efficiencies of 0.4%, 4.2%, and 7.4% at 1550 nm in diffusion transport dominated devices. The remarkable increase in $L_{\text{diff}}$ from 60 nm to 115 nm after exposure to ambient conditions for 36 days coincides with an increase in untrapped excess carrier lifetime in the CQD film. However, it cannot be concluded that the increase in diffusion length is a consequence of increased untrapped carrier lifetime alone.

The measured diffusion lengths are comparable to the depletion widths in CQD Schottky barrier devices, indicating that diffusion currents represent a significant proportion of the observed photocurrent in this class of photodiode. Further improvements in PbS CQD photodiode EQE can be expected through increases in diffusion length, making this a critical parameter for sensitivity optimization.
Chapter 7. Sensitive, Megahertz-Bandwidth CQD Photodiodes

7.1 Introduction

The model of CQD photodiode operation and subsequent measurement of the diffusion current indicated that an even faster CQD photodiode could be developed if photocarriers could be transported by drift alone. This could be accomplished by developing photodiodes with fully-depleted CQD films. Fabrication and characterization of such CQD photodetectors yielded a dramatic increase in device operating speed.

A consequence of the elimination of the diffusion component of the photocurrent in CQD photodiodes is reduced EQE and sensitivity. To offset this, optical strategies were investigated to pass incident light sequentially through multiple CQD photodiodes, effectively increasing the optical density of the collective structure.
7.2 Fully-Depleted CQD Photodiodes

7.2.1 Device Architecture

Fully-depleted semiconductor films are the basis of high-speed p-i-n photodiodes implemented in crystalline semiconductors. A region of semiconductor material with a very low (intrinsic) doping level is used to create a wide depletion region between thinner p- and n-doped regions. The majority of photocarrier generation takes place in the intrinsic region where drift transport dominates. In a Schottky barrier photodiode, the width of the depletion region can be maximized through the use of very low semiconductor doping levels, however, the potential barrier height may be reduced.

In CQD photodetectors, effective doping of the semiconductor is accomplished through the oxidation of PbS. By reducing the degree of oxidation of the CQD film (by limiting exposure to ambient conditions), less doping is expected and the maximum depletion width for a given Schottky barrier is realized.

Only small gains in depletion width were achieved through reduced oxidation. To created fully-depleted devices, the CQD film width was reduced to equal the depletion width (180 nm). Other than reduced film thickness, the fully-depleted CQD photodetectors retain the same device architecture as the original CQD photodiode discussed in Chapter 5. A cross-sectional representation of the fully-depleted CQD photodiode is presented in Figure 7.1a.
Figure 7.1. (a) Schematic, cross-sectional representation of the CQD Schottky barrier diode architecture. (b) Energy bands in the PbS CQD film near the Schottky barrier at the Al/PbS interface. Electrons and holes generated in the depletion region ($G_{DR}$) drift under the influence of the built-in electric field of the junction to the Al contact and ITO contact, respectively.

In a fully-depleted photodiode all photogenerated electrons and holes are swept to the contacts by the electric field resulting from the built-in potential of the junction and any externally applied bias. The diffusive and relaxation transport mechanisms of the minority and majority carriers associated with the quasi-neutral region are eliminated, as shown in Figure 7.1b.

### 7.2.2 Transient Response and 3dB Frequency Increase

The response of the fully-depleted CQD photodiode to changes in illumination is limited only by the drift transit time (~300 ns), as indicated by the transient photocurrent response to a 1 μs square illumination pulse shown in Figure 7.2. The response times of
CQD photodiodes with a diffusion current component are \(~200 \, \mu s\) (Sections 5.6.1 and 6.4.2), approximately three orders of magnitude longer.

Reduction of the photodiode response time resulted in an extension of the substantially flat frequency response to beyond 100 kHz and a 3dB frequency ranging from 1.6 MHz at zero bias to nearly 3 MHz at -5 V bias, as shown in Figures 7.3a and 7.3b. The bias dependence of the response speed derives from a linear reduction in carrier transit time with increasing electric field in the depletion region.

The drift transit time of the fully-depleted CQD photodiode was further reduced by increasing the mobility of the CQD film through a more complete ligand exchange than that used in the initial photodiode development. Majority carrier hole mobility increased from \(10^{-4} \, \text{cm}^2.\text{V}^{-1}.\text{s}^{-1}\) to \(6\times10^{-4} \, \text{cm}^2.\text{V}^{-1}.\text{s}^{-1}\).
7.2.3 Additional Device Characterization

I-V Characteristics

The fully-depleted CQD photodiode maintained the $I-V$ characteristics of the original CQD photodiode. Figure 7.4a and 7.4b shows the steady-state current-voltage ($I-V$) characteristics in the dark and at 17.9 $\mu$W.cm$^2$ illumination at 1550 nm. Rectification greater than 450x was observed at +/- 0.5 V bias.
Photoresponse and Sensitivity

Initial testing of the fully-depleted CQD photodiode showed a decrease in EQE from 17% to 13% at the first excitonic feature, compared to the original CQD photodiode. Reduction in CQD film thickness resulted in a decrease in the total charge collection volume of the film and a net decrease in photoconversion efficiency.

Ongoing refinements in CQD synthesis and processing resulted in an increase in the EQE of the fully-depleted CQD photodiodes to 21% at the first excitonic feature and up to 50% in the visible. The spectral dependence of EQE and D* of the improved fully-depleted device are shown in Figure 7.5. D* at 295K exceeds $2 \times 10^{11}$ Jones at both the excitonic absorption peak and in the visible.

Figure 7.4. Steady-state $I-V$ characteristics in the dark and with 17.9 $\mu$W.cm$^{-2}$ illumination at 1550 nm on (a) linear and (b) log scales.
Figure 7.5. EQE and normalized detectivity as a function of wavelength (295 K).

Figure 7.6a shows EQE increasing superlinearly with reverse bias. The existing photodiode model does not capture this dependency, as all carriers generated in the depletion region are assumed to be extracted before they recombine. Two possible explanations for this phenomenon remain untested: increased carrier extraction efficiency resulting from changes in trap occupancy in the CQD film with increasing reverse bias, or illumination modulated injection of holes at the Al contact resulting from barrier thinning with increased reverse bias. Breakdown of these devices occurs between -3 V and -5 V.

Similar to the original CQD photodiode, the photoresponse of the fully-depleted CQD photodiode remains linear within 10% over 6 decades of irradiance. Dark current was unchanged from the original devices at 0.1 nA.cm\(^{-2}\).
Figure 7.6. (a) EQE as a function of reverse bias. (b) Photocurrent density as a function of irradiance.

7.3 Multi-Pass, Fully-Depleted CQD Photodiodes

7.3.1 Increasing Effective Optical Density

Fully-depleted CQD photodiodes demonstrate increased operating speed by limiting carrier generation to the depletion region of the Schottky barrier. The resulting ultra-thin devices lack the optical density required to absorb the majority of incident radiation. This effect is especially evident at the excitonic absorption wavelengths, where absorption coefficients are lower than at visible wavelengths.

Depletion region widths in the CQD photodiodes were observed to be relatively invariant to variation in post-ligand-exchange film treatment. Assuming that the width of the depletion region and the CQD film thickness were fixed, methods to increase the optical path length in the film were investigated. These approaches would maintain the fully-depleted CQD photodiode architecture and its fast response speed. Increased path length
could be obtained through scattering in the CQD film or at the reflective contact, multiple
passes through a single CQD film, or multiple passes through multiple CQD films. For
the current study, we focused on multiple illumination passes through films where the
effect of each pass on illumination power could be quantified.

**Transparent Schottky Barriers**

If the both contacts used in the CQD photodiode were transparent, devices could be
stacked, allowing incident illumination to pass through multiple devices until it was
completely absorbed. Development of transmissive Schottky contacts was investigated,
but suitable combinations of work function and transparency across the visible and IR
were not obtained. Devices exhibited either good Schottky barrier characteristics and
poor transmission (~10%), or high transmission (~80%) and insufficient built-in potential
to efficiently separate photogenerated carriers.

This study was limited to materials deposited from thermal and non-reactive DC
sputtered sources. Low-workfunction transparent oxides such as zinc oxide were not
tried due to practical limitations, but could prove to be an effective means to fabricate a
transparent Schottky barrier to a CQD film.

**Sequential Absorption with Multiple Devices**

A simpler route to demonstrate the advantage of multiple absorption passes through CQD
films is to create an optical sequence through multiple CQD photodiodes. This strategy
makes use of the fully-depleted CQD photodiodes already developed and is intended to
serve as a precursor to development of an integrated multi-junction photovoltaic device. To determine the feasibility of this strategy, detailed measurements of CQD film and device reflectance were performed.

### 7.3.2 Reflection from CQD Films and CQD Photodiodes

Reflectance measurements indicated that a large proportion of the light incident on a fully-depleted CQD photodiode was back-reflected by the numerous materials interfaces and the highly reflective Al contact. Figure 7.7 shows CQD film and fully-depleted CQD photodiode reflectance as a function of wavelength. Measurements of the CQD film on an ITO coated glass substrate (identical to that used for device fabrication) showed primarily specular reflection across the visible and near IR. At 1550 nm, 33% of incident light was reflected specularly and an additional 3% reflected diffusely. Addition of an aluminum contact to complete the CQD photodiode increased specular reflection to 51% +/- 3% at 1550 nm.
7.3.3 Multi-Pass Device Architecture

To allow sequential illumination of identical fully-depleted CQD photodiodes, an architecture based on photodiodes fabricated on a single substrate (and single CQD film) was developed. A schematic representation of the multi-pass CQD photodiode architecture is shown in Figure 7.8a. Incident illumination is directed onto device 1. The light reflected back from this device is redirected onto device 2 by a mirror, mounted parallel to the photodiode substrate. This structure can be extended indefinitely, allowing light to be passed sequentially through a large number of photodiodes.

Collimated laser illumination provides a small diameter beam (1.5 mm) allowing the path of light to be precisely controlled for quantification of the efficiency of the double-pass photodiode architecture. Larger Al contacts (1.58 mm diameter) than those used in
previous CQD photodiodes (0.8 mm diameter) allowed better control of illumination capture and reflection from the individual devices. Note that angle of incident illumination is exaggerated in Figure 7.8a: actual illumination was incident at ~1 degree off normal.

As the photodiodes are operated in a current sensing mode, they are connected in parallel electrically to allow their signals to combine additively. This connection results in a multi-pass structure with an electrically active area 2x larger than the individual photodetectors.

Figure 7.8. (a) Schematic, cross-sectional representation of the CQD Schottky barrier diode architecture and the double-pass of incident illumination through devices 1 and 2. (b) Energy bands in the PbS CQD film near the Schottky barrier at the Al/PbS interface. Electrons and holes generated in the depletion region ($G_{DR}$) drift under the influence of the built-in electric field of the junction to the Al contact and ITO contact, respectively.
7.3.4 EQE and Sensitivity Enhancement

Table 7.1 summarizes the EQE and sensitivity of the individual fully-depleted CQD photodiodes and two devices connected in parallel electrically. At ~22%, the individual devices already demonstrated record EQE at the first excitonic absorption peak (for fully-depleted devices). Sequential absorption increased EQE to 34%; an improvement of 56%. This is in good agreement with the 51% +/-3% measured reflection of incident irradiance from the fully-depleted CQD photodiode. D* increased by 7% from 1.2x10^{11} Jones to 1.3x10^{11} for the individual and connected devices, respectively.

Table 7.1. Photodiode response and sensitivity at 1550 nm illumination.

<table>
<thead>
<tr>
<th>Device</th>
<th>EQE [%]</th>
<th>$i_{\text{noise}}$ [fA.Hz^{1/2}]</th>
<th>D* [Jones]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 or 2</td>
<td>22</td>
<td>312</td>
<td>1.2x10^{11}</td>
</tr>
<tr>
<td>1 &amp; 2</td>
<td>34</td>
<td>454</td>
<td>1.3x10^{11}</td>
</tr>
</tbody>
</table>

7.3.5 Additional Device Characterization

Current-Voltage Characteristics

The fully-depleted CQD photodiodes prepared for this study maintained the $I-V$ characteristics of CQD photodiodes observed previously. Figure 7.9a and 7.9b show the steady-state current-voltage ($I-V$) characteristics in the dark and at 17.9 μW.cm$^{-2}$ illumination at 1550 nm. Rectification greater than 350x was observed at +/- 0.5 V bias.
Figure 7.9. Steady-state $I-V$ characteristics in the dark and with 17.9 $\mu$W.cm$^{-2}$ illumination at 1550 nm on (a) linear and (b) log scales.

**Transient Photocurrent and Frequency Response**

Fully-depleted CQD photodiodes demonstrated longer response times than devices with smaller Al contacts prepared for the study in Section 7.2. Figure 7.10a and 7.10b show transient responses of the individual and connected photodiodes to a 5 $\mu$s square 1550 nm illumination pulse at 0.5 mW.cm$^{-2}$. The response times of these devices are still nearly two orders of magnitude shorter than the diffusion limited response times of the original CQD photodiodes.

The transient response of these CQD photodetectors appears to be RC-limited with a timeconstant of $\sim$1 us. The normalized photocurrent transients of devices 1 and 2, shown in Figure 7.10b, are nearly identical. When connected in parallel, the timeconstant increases. This RC-limited photoresponse is similar to that observed in thin-film organic photodiodes with increasing device area$^{16}$ (See Appendix C for details).
Figure 7.10. Photodiode transient response to a 5 μs square 1550 nm illumination pulse at 0.5 mW.cm$^{-2}$.

The 3dB frequency of the individual photodetectors ranged from 0.48 MHz at zero bias to 1.6 MHz at -3 V bias, as shown in Figures 7.11a and 7.11b. When connected to form the multi-pass device, the 3dB frequency at zero bias dropped to 0.36 MHz, but was similar to the individual devices when reverse bias was applied. The bias dependence of the 3dB frequency is sub-linear, in contrast to the highly linear dependence observed in the fully-depleted CQD photodiodes with transport limited photoresponse. A much larger (300% vs. 44%) increase in 3dB frequency is also observed with application of -3V of reverse bias.
7.3.6 Sensitivity Limitations of the Multi-Pass Architecture

The multi-pass photodiode architecture demonstrates a significant increase in EQE but a much smaller increase in sensitivity, as represented by $D^*$. This is due to the increase in device electrical area and associated internal noise. For a 50% increase in responsivity with a 100% increase in device area, a theoretical limit on the improvement in $D^*$ can be calculated. Assuming detector noise derives solely from thermal sources (Section 2.1.2),

$$i_{noise} = \sqrt{\frac{4k_BT\Delta f}{R_o}}, \quad (7.1)$$

a 2 fold increase in device area results in a 2 fold decrease in $R_o$ and a $\sqrt{2}$ fold increase in noise current. The noise equivalent power,

$$NEP = \frac{i_n}{R_i}, \quad (7.2)$$
decreases by $\sqrt{2}/1.5$, or 6%. Normalizing for detector area, assuming that the optically active area of the detector remains unchanged (only the electrically active area increases),

$$D^* = \frac{\sqrt{A\Delta f}}{NEP},$$

(7.3)

D* increases by only 6%.

### 7.4 Conclusions

The response speed of the fully-depleted CQD photodiode represents a substantial improvement over all reported CQD photodetectors: a 170,000 fold improvement in response speed over the most sensitive CQD photodetector reported\(^1\), and a nearly 50 fold improvement in response speed over the fastest CQD photodetector reported\(^2\). With D* $>10^{11}$ Jones at room temperature, this device maintains a 10,000 fold improvement in sensitivity over the fastest CQD photodetector reported\(^2\).

The combination of speed and sensitivity demonstrated by the fully-depleted CQD photodiode represents a $>1000$ fold improvement in sensitivity*bandwidth product relative to all previous CQD photodetectors. This improvement in device performance was achieved by designing a photodiode architecture to take advantage of insights into charge carrier transport and by tailoring the CQD film passivation to support both high carrier mobilities and a large built-in potential at a metallurgical junction. The fully-depleted architecture provides a simple route to fabrication of high sensitivity, high speed photodetectors based on CQD films.
Harvesting the light that would otherwise be back-reflected by a single CQD photodiode allowed multi-pass fully-depleted CQD photodiode structures to increase overall EQE by 56% at the first excitonic absorption feature. A two-stage multi-pass device demonstrated an EQE of 34% at 1550 nm while maintaining operating bandwidth greater than 1 MHz. This proof-of concept device indicates the feasibility of fabricating multiply-stacked CQD photodiode structures on a single substrate that demonstrate both megahertz operating speed and high efficiency. Additionally, these techniques can also be applied to CQD photodiodes with both drift and diffusion photocurrent components to create devices with optimal EQE and sensitivity, operating at diffusion response limited speeds. However, ultimate performance, including sensitivity, will require increasing the absorption coefficient of the CQD film or increasing the drift-only photocharge collection volume of the CQD photodetector without increasing the electrical area of the device.
Chapter 8. Conclusions and Recommendations for Future Work

8.1 Sensitive, Megahertz-Bandwidth Spectrally-Tunable CQD Photodetectors

The present work reports highly sensitive, spectrally-tunable photodetectors operating across the visible and the short-wavelength IR exhibiting 3 MHz bandwidth, normalized detectivity \((D^*) > 10^{12}\) Jones, and dark current density of 0.1 nA.cm\(^{-2}\). This represents a >100,000 fold improvement in response speed and an 11 order-of-magnitude reduction in dark current density over the most sensitive CQD photodetector reported\(^1\). It represents a 100,000 fold improvement in sensitivity and a nearly 50 fold improvement in response speed over the fastest CQD photodetector reported\(^2\).

This improvement in device performance was achieved by first addressing the primary requirements of a sensitive, efficient photodiode: a large built-in potential to separate photogenerated charge carriers and minimize internal noise generation, and high semiconductor conductivity for efficient collection of photogenerated charge. Schottky barriers to CQD films were developed to provide high, uniform built-in potentials. A multi-step CQD ligand exchange procedure was developed to allow deposition of uniform, tightly packed films of CQDs with high mobility and to eliminate chemical interactions with the aluminum contact forming the Schottky barrier. A stable
metallurgical junction at the rectifying contact was found to be essential for minimizing noise and maximizing device lifetime.

Detailed characterization of the Schottky barriers and the photoresponse of the CQD photodiodes provided insight into the physical mechanisms underlying their operation. Identification and measurement of separate drift and diffusion components in the temporal response of the photodetectors lead to the development of a numerical model of device operation. This model successfully predicted device performance based on measurable physical parameters of the CQD photodiode.

Based on this understanding of CQD photodiode operation, optimized devices that excluded the slow diffusive component were fabricated, exploiting only the sub-microsecond field-driven transient to achieve MHz response bandwidth. The efficiency of the resulting devices was limited by low optical density. Further improvements in photodiode efficiency were demonstrated through the use of a multi-pass device architecture to increase the fraction of incident light collected.

Three different regimes of device operating speed were observed. In the original CQD photodiodes, response speed was limited by charge carrier diffusion. Elimination of the diffusion current revealed that response speed could be limited either by charge carrier drift under the influence of an electric field, or RC-limited by the capacitance of the parallel plate device geometry and the resistance of the CQD film.
This work demonstrated development of an understanding of the mechanisms governing CQD photodiode operation and control over the parameters that determine device performance. The operating speed limitations of previous photoconductive CQD photodetectors were readily eclipsed by adoption of a photovoltaic detector architecture. The sensitivity limitations of previous solution-processed photovoltaic detectors were addressed through development of a metallurgical junction to a CQD film with a high, uniform potential barrier and through optimization of photogenerated charge carrier transport in the CQD film. By combining understanding of device operation and materials control, record speed and sensitivity were achieved in solution-processed broadband photodetectors.

8.2 Further Development of CQD Photodiodes

Further development of CQD photodiodes could focus on improving the EQE of individual fully-depleted devices by increasing the width of the depletion layer. In principle, this could be accomplished by reducing the doping of the CQD film. However, the potential barrier at the Schottky contact would have to be maintained in order to preserve the built-in potential necessary for efficient photogenerated charge carrier separation and limiting internal noise. These requirements may be obtainable through further development of the CQD surface modification strategy, possibly using alternative ligands, or finer control of the oxidation states of the CQD surfaces.

If significant improvements in depletion width are not feasible, further development of multiple photodiodes in a stacked architecture may be the best alternative for developing
the most sensitive, fast CQD photodiodes. To avoid losses due to reflection at interfaces to the CQD film, anti-reflective treatments such as surface texturing may be beneficial. These interfaces also serve as electrical contacts; any additional materials used to suppress reflections must be conductive and have an appropriate work function for the intended type of contact.

To understand better the role of device exposure to ambient conditions, a study of the Schottky barrier characteristics as a function of exposure to an ambient atmosphere could be undertaken. This study could also address the effects of the benzene dithiol treatment on the physical parameters of the metallurgical junction.

Finally, large-scale integration of CQD photodiodes with Si microelectronics would complete the initial direction of this study, demonstrating an IR sensitive, monolithically integrated imaging array. Assuming the performance of CQD photodiodes would be maintained or improved upon, such an array would be capable of SWIR imaging using only naturally occurring airglow illumination. All of the response time issues encountered with photoconductive CQD photodetectors would be eliminated, allowing image capture with sub-microsecond exposure.
Bibliography


Dark current under short circuit conditions is below a measurable limit of 0.1 nA.cm^-2 determined by the voltage overburden of the instrumentation (20 uV) and the effective shunt resistance of the photodiode (8 MOhm).


Appendix A. Experimental Methodology

A.1 Synthesis and Fabrication

A.1.1 Low Power ITO Sputtering

Low power sputtered deposition of ITO was performed using a BOC Edwards AUTO 306 vacuum deposition system fitted with a DC magnetron source. Inert Ar gas and ceramic ITO targets were found to provide highly conductive and transmissive ITO films without introduction of reactive gases.

A.1.2 PbS CQD Synthesis

PbS CQDs with an excitonic peak ~1500 nm were prepared by injection of 2.0 mmol bis(trimethylsilylsulphide) into a reaction flask containing 4.0 mmol lead oxide (0.9 g), 9.5 mmol oleic acid (2.67 g) and 18.8 mmol octadecene (4.73 g) at 120°C. After the injection, the reaction was quenched by moving the flask to an ice-water bath.

The synthesis was carried out under inert conditions using a Schlenk line. The final PbS oleate-capped CQDs were isolated from any remaining starting materials and side products by precipitating with acetone and re-dissolving in toluene, repeated 2x.

A.1.3 Primary Butylamine Ligand Exchange

Solution-phase ligand exchange required precipitating the CQDs with MeOH and redissolving in toluene 2x before a final precipitation with MeOH and redissolving in primary butylamine. The mixture was left for 3 days at room temperature, then
precipitated with isopropanol and redispersed in octane. All processing was carried out in a glove box with an N2 atmosphere.

**A.1.4 CQD Film Deposition**

Films were formed by spin-coating CQDs suspended in octane onto commercial glass substrates coated with conductive indium-tin oxide (ITO). Solution density and spin velocity were varied to obtain the desired film thickness. All CQD film deposition was carried out in an inert environment.

**A.1.5 Benzene Dithiol Treatment**

After film deposition, the CQDs were treated in a 5mg/ml solution of benzene dithiol (BDT) in acetonitrile for up to 60 min. BDT treatment and subsequent film handling was performed under ambient conditions.

**A.1.6 Aluminum Contact Deposition**

Aluminum contacts (100 nm thick, 1.96 mm² area) were deposited on top of the CQD films by thermal evaporation of metal aluminum sources at ~10⁻⁵ Torr at a rate of ~0.5 nm.s⁻¹ using a BOC Edwards AUTO 306 vacuum deposition system.

**A.1.7 Ambient Annealing**

The complete CQD photodetectors were exposed to a high-humidity air atmosphere at 35C for up to 12 hours to accelerate oxidation of the CQD film.
A.2 Characterization

A.2.1 Monochromatic Photoresponse

Devices were illuminated through the glass substrate and ITO transparent contact. Uniform illumination was provided by a Roithner Lasertechnik 1550 nm LED array with an Agilent 33220A 20 MHz function generator used to supply a constant or modulated bias to the LEDs. The irradiance was calibrated using a Newport 2930C power meter and 918-IG calibrated photodetector placed at the position of the CQD photodiode. Steady-state current was measured with a Keithley 6430 sub-femtoamp SourceMeter and transient currents were measured with a Stanford Research SR570 low-noise-current preamplifier and a Tektronix TDS 220 or TDS 5104 digital oscilloscope. Biases, if used, were supplied by the SourceMeter or current preamplifier. Frequency, wavelength, and illumination dependencies of the photocurrent were measured with a Stanford Research SR830 lock-in amplifier in current measurement mode. All measurements were performed in a dark, shielded enclosure at room temperature (295 K) in air, except for the temperature-controlled measurements which were measured in an N₂ atmosphere using a liquid nitrogen bath cryostat.

High-speed characterization of the fully-depleted CQD photodiode utilized a JDS Uniphase SWS15101 Tunable Laser Source modulated by an Agilent 33220A 20 MHz function generator. The rise and fall time of the laser was measured at 40 ns and 60 ns, respectively. Photocurrent was measured using a 25 Ohm resistive load as a transimpedance stage and a Tektronix TDS 5104 digital oscilloscope. High illumination intensities (40 mW.cm⁻²) were used to provide suitable signal-to-noise ratios for measurements.

A.2.2 Spectral Photoresponse

Monochromatic illumination was provided by a Jobin Yvon Triax 320 monochromator with a ScienceTech TH-PS white light source. Multimode optical fibers were used to direct the light to a collimator and the CQD photodiode. Incident irradiance was
invariant within 4% from 400 to 1800 nm. The light was mechanically chopped at 100 Hz and the photocurrent response at zero bias was recorded with a Stanford Research SR830 lock-in amplifier. The spectral photocurrent was scaled to match the monochromatic response measured at 1550 nm. All measurements were performed in a dark, shielded enclosure at room temperature.

A.2.3 Noise Current
Noise was measured in the dark, at zero bias, using a Stanford Research SR830 Lock-in Amplifier in current measurement mode. Noise current was measured directly using the lock-in amplifier and normalized by the input bandwidth. All measurements were performed in a dark, shielded enclosure at room temperature (295 K) in air, except for the temperature-controlled measurements which were measured in an N₂ atmosphere using a liquid nitrogen bath cryostat.

A.2.4 CQD Film and Photodiode Absorption and Reflectance
The photodiode was placed in an integrating sphere and illuminated directly using a calibrated source. All light reflected back by the various dielectric interfaces or the Al back contact was captured by the integrating sphere, yielding the net absorption of the complete device structure. By measuring, separately, the absorption of the complete photodiode, the glass/ITO substrate, and an isolated Al contact, the net absorption in the CQD film was calculated. All measurements were performed with a Varian CARY 500 UV-Vis-NIR spectrometer using an integrating sphere accessory module. Reflection mode was used for all measurements and both spectral and diffuse reflections were collected from the sample. CQD film spectral reflectance was measured similarly using the integrating sphere.

A.2.5 Temperature Controlled Measurements
Temperature controlled measurements were conducted with the CQD photodiode mounted on a steel chuck with a resistive heating element and placed in a liquid nitrogen
A Lakeshore 331S temperature controller was used to control the resistive heater. A multimode fiber was used to direct illumination from a Roithner Lasertek 1550 nm LED diode array. Device characteristics were measured as described in the Methods.

**A.2.6 Carrier Extraction by Linearly Increasing Voltage (CELIV)**

CQD photodiodes were connected in series with a bias source and resistive load. The linearly increasing device bias was provided by an Agilent 33220A 20 MHz function generator and the transient currents measured with a Tektronixs TDS 220 digital oscilloscope across the resistive load (typically 50 Ohms). All measurements were performed in a dark, electrically shielded enclosure.

**A.2.7 Capacitance-Voltage (CV)**

Capacitance measurements were performed using an Agilent 4284A LCR meter with a 10 mV probe signal modulated at 20 Hz. Any applied bias was supplied by the LCR meter. All measurements were performed in a dark, electrically shielded enclosure.

**A.2.8 Open-Circuit Voltage Decay (OCVD)**

Uniform illumination was provided by a Roithner Lasertechnik 1550 nm LED array with an Agilent 33220A 20 MHz function generator used to supply a modulated bias to the LEDs. A Tektronixs TDS 5104 digital oscilloscope with at 1 MΩ input impedance was used to measure the open-circuit voltage transient decay of the samples.

**A.2.9 Quasi-Steady-State Photoluminescence (QSSPL)**

Quasi-steady-state photoluminescence measurements were performed at room temperature using the 633 nm line of a HeNe laser with an irradiance of approximately 10 mW.cm². A 1 mm diameter beam provided a large sample area to offset any inhomogeneities in the spincoast CQD films. PL emission was measured using a fibre-coupled Ocean Optics NIR-512 spectrometer with a cooled detector at -5°C.
Measurements were taken at 10s intervals over a 5 minute period to ensure steady-state conditions were achieved. At least two measurements at different locations were captured for each film at each processing step.

A.2.10 Steady-State Photocarrier Grating (SSPG)

SSPG measurements were performed on a CQD film spun-cast on a glass substrate with parallel Au contacts (spacing 100 μm). A JDS Uniphase 633 nm HeNe laser, beamsplitter, half-wavelength plate, neutral density filter, and two mirrors were used to create the photograting on the CQD film. A PTI OC-4000 mechanical chopper was used to break the path of the low-irradiance beam (2 Hz modulation). A DC bias (20 V) was provided by a Keithley 2400 SourceMeter, and the modulated photocurrent was measured with a resistive load and a Stanford Research SR830 lock-in amplifier.

A.2.11 Time-of-Flight (TOF)

Pulsed illumination was provided by a Quantronix Darwin Nd:YLF laser operating at 527 nm and producing 150 ns pulses at a 1 kHz repetition rate. Photodiode bias was provided by a Keithley 2410 SourceMeter, and the photocurrent transient was measured using a Tektronixs TDS 5104 digital oscilloscope with a 50 Ω resistive load. All measurements were performed in a dark, electrically shielded enclosure.

A.2.12 X-ray Photoelectron Spectroscopy (XPS)

CQD film samples for XPS analysis were spin-cast on Au overcoated Si substrates. Immediately following any film treatment, the samples were transferred to high vacuum (~10⁻⁹ Torr) for analysis. XPS measurements were performed using a PHI 5500 ESCA (XPS)/ISS system. XPS spectra were generated by an Al Kα source with a photon energy of 1486.6 eV and recorded at a photoelectron take-off angle of 45 degrees to enhance surface sensitivity. The sample analysis area is ~0.5 mm² at a dept of ~6 nm from the surface.
Appendix B. External Quantum Efficiency of CQD Photodiodes

B.1 Introduction

The external quantum efficiency of the CQD photodiode is a product of three separate processes, each characterized by a fractional efficiency,

$$\eta_{\text{external}} = \eta_{\text{abs}} \cdot \eta_{\text{diss}} \cdot \eta_{\text{extr}}.$$  

The absorption efficiency, $\eta_{\text{abs}}$, is the fraction of the incident photon flux absorbed by the CQD film. The two remaining efficiency terms represent photogenerated charge carrier dynamics on two very distinct timescales. The dissociation efficiency, $\eta_{\text{diss}}$, represents the probability of photogenerated excitons dissociating into individual charge carriers. The extraction efficiency, $\eta_{\text{extr}}$, quantifies the fraction of charge carriers transported, through drift and diffusion, to their extracting contacts before recombining. Both $\eta_{\text{diss}}$ and $\eta_{\text{extr}}$ are significantly influenced by the presence of traps in the CQD film.

Figure B.1 shows the fundamental processes governing the behaviour of charge carriers in the CQD film:

1. Optical generation of an exciton within a CQD  
2. Dissociation of the exciton, assisted by shallow traps, into an electron-hole pair  
3. Transport of charge carriers between CQDs  
4. Possible deep trapping of electrons and subsequent recombination.
Figure B.1. Generation, dissociation, trapping and recombination in the CQD film.

**B.2 Absorption Efficiency**

The absorption efficiency is calculated from the fraction of incident irradiance reaching the CQD film and the exponential decay of irradiance in the film,

\[ \eta_{abs} = T_{sub} (1 - e^{-\alpha d}), \]  

(11.1)

where \( T_{sub} \) is the net transmittance of the transparent substrate and ITO contact, \( \alpha \) is the measured absorption coefficient of CQD film, and \( d \) is the effective illumination path length in the film.

In the case of the original CQD photodiode, with a substrate transmittance of 85%, film thickness of 340 nm and effective double pass through the film due to the reflective Al
contact, $\eta_{\text{abs}} \sim 37\%$ at the excitonic absorption feature (1450 nm) and $\eta_{\text{abs}} > 80\%$ at 500 nm.

### B.3 Dissociation Efficiency

The dissociation efficiency, $\eta_{\text{diss}}$, represents the probability of photogenerated excitons dissociating into individual charge carriers. The dissociation efficiency captures carrier behavior on the radiative lifetime timescale – typically on the order of nanoseconds.

Excitons generated by the absorption of photons are prone to recombine before dissociating into individual charge carriers. Shallow traps on the surfaces of the CQDs are expected to increase exciton radiative lifetime, preventing recombination of photogenerated carriers before excitons dissociate into separate charge carriers. Radiative lifetimes in PbSe and PbS CQD films have been measured over a range of $<100$ ns up to 0.8 ms and 1.0 ms$^{100,121-123}$, respectively, with the longest lifetimes attributed to the effects of trapping$^{124}$.

Radiative lifetimes in lead chalcogenide CQDs are also significantly higher than in cadmium chalcogenide CQDs due to dielectric screening – owing to the much higher dielectric permittivity of these materials$^{100}$.

While absorption efficiency and extraction efficiency can be calculated from measured physical properties of the CQD film and photodiode, dissociation efficiency is determined from the fit of the model results to the measured steady-state photocurrent. At irradiances up to $\sim 10^{-5}$ W.cm$^2$, extraction efficiency is $\sim 100\%$ (discussed below). Under these conditions, dissociation efficiency lies in the range 39%-57%, depending on bias, to account for the observed external EQE of 17% to 25% at the excitonic absorption feature (1450 nm) over the bias range 0.0 to -1.0 V. The bias dependence of $\eta_{\text{diss}}$ is attributed to field-assisted exciton dissociation and variation in shallow trap occupancy.
B.4 Extraction Efficiency

The extraction efficiency is determined by the lifespan of individual carriers – on the order of microseconds – and the transport time of the device. As transport time depends on the dominant transport mechanism, drift or diffusion, it must be calculated separately for the depletion region and quasi-neutral region of the CQD photodiode.

Electrons have the potential to be captured by deep, long-lived traps where they ultimately recombine. Only the fraction of electrons that avoid capture in deep-traps can contribute to the photocurrent. Minority carrier (electron) traps in CQD films have lifetimes of 30 +/- 20 ms, as determined from detailed studies of the photoconductive response of thiol treated PbS CQD films\textsuperscript{77}. At low illumination modulation frequencies (<100 Hz) the effect of recombination of carriers in these traps is apparent in the temporal response of the photocurrent, which decay with timeconstants on the order of 1 to 100 milliseconds, depending on irradiance. At higher illumination modulation frequencies, the rates of capture and recombination in the traps maintain a steady state trap population and the effect of carrier trapping and recombination is a reduction in the fraction of photogenerated charge carriers extracted at the contacts.

B.4.1 Depletion Region

The transit time of the depletion region is in the range of 10 $\mu$s to 300 ns, depending on the depletion region width, the charge carrier mobilities, and the internal electric field. Increasing reverse bias reduces carrier transit time – as evidenced by increasing 3dB frequencies. However, under all measured conditions, the depletion region transit time (drift time) is significantly less than the measured carrier lifetime, as shown in Figure 11.2b. This results in 100% extraction efficiency from the depletion region for all measured irradiances.

In the original CQD device, increasing the reverse bias also increases the width of the depletion region. Transport via drift occurs over a greater proportion of the volume of
the CQD film resulting in a reduction of the net contribution of effects derived from transport in the quasi-neutral region.

**B.4.2 Quasi-Neutral Region**

Extraction efficiency in the quasi-neutral region of the CQD photodiode is limited by the diffusion length of minority carrier electrons in the CQD film, which depends on the carrier lifetime.

As shown in figure 11.2b, for a 340 nm thick CQD film with a 180 nm thick quasi-neutral region, the quasi-neutral region transit time (diffusion time) is less than the carrier lifetime at irradiances up to $\sim 10^{-5}$ W.cm$^2$. At these irradiances, diffusion is effective in transporting minority carrier electrons to the edge of the depletion region before they recombine. Under these conditions, diffusion extraction efficiency is $\sim 100\%$, as shown in Figure 11.2a.

At irradiances in excess of $\sim 10^{-5}$ W.cm$^2$, carrier lifetime becomes comparable to the quasi-neutral region transit time and extraction efficiency in the quasi-neutral region begins to decrease. This corresponds to the observed reduction in the quantum efficiency of the CQD photodiode, as shown in Figure 3c in the manuscript.

Increasing the CQD film thickness also results in a decrease in the quantum efficiency of the CQD photodiode. The optimal device film thickness of $\sim 350$ nm was determined empirically to yield the highest EQE over the range of irradiances of interest for the photodetector.
Figure B.2. Extraction efficiency and carrier lifetime dependence on irradiance. (a) Drift and diffusion extraction efficiency as a function of irradiance. (b) Measured carrier lifetime, depletion region transport time (drift time), and quasi-neutral region transport time (diffusion time) as a function of irradiance.
Appendix C. RC-Limited Photoresponse of Fully-Depleted CQD Photodiodes

The area of the fully-depleted CQD photodiodes used in the multi-pass architecture in Section 7.3 is 0.02 cm\(^2\); four times the area of the device presented in Section 7.2. This results in a 4 fold increase in capacitance. However, it is not likely that the increase in capacitance is sufficient, on its own, to explain the transition from transport-limited photoresponse to RC-limited photoresponse observed between these two devices.

When the device area and capacitance of the larger fully-depleted CQD photodetectors is doubled, by connecting them in parallel, only a small increase in the timeconstant is observed. The external resistive load was held constant at 25 Ohms. This indicates that the photoresponse time constant is heavily influenced by the internal resistance of the photodetectors as well as their capacitance. The decrease in internal device resistance, which is inversely proportional to device area, offsets the increase in capacitance when the two devices are connected in parallel.

The timeconstant of the larger fully-depleted CQD photodetectors, and DC conductivity under reverse bias, were observed to depend on incident irradiance. The timeconstant decreased and the conductivity increased with increasing irradiance, both consistent with increasing conductivity. The changes in conductivity in response to a change in irradiance took place on the order of seconds, consistent with photoconductive response of the CQD films. To investigate this phenomenon quantitatively, the roles of the Schottky barrier and the CQD film in determining effective device conductivity would need to be deconvolved.
Appendix D. Publications Related to the Thesis

D.1 In Preparation


D.2 Refereed Journals


### D.3 Refereed Conference Proceedings

Hoogland, S. et al., 25% Modulation Depth at 1.54 μm from Large-Area Solution-Processed Colloidal Quantum Dot Electro-Absorption Modulators, in *CLEO 2007*, post-deadline submission. (Baltimore, MD, May 2007).

### D.4 Invited Conference Presentations

J. Clifford, High Performance Colloidal Quantum Dot Optoelectronic Devices, in *Particles 2007*, sponsored by the Division of Colloid and Surface Chemistry of the American Chemical Society. (Toronto, Canada, August 2007).