Proton Irradiation Effects on Semiconductor CdSe/ZnS Core/Shell Nanocrystals

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Proton Irradiation Effects on Semiconductor CdSe/ZnS Core/Shell Nanocrystals
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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Microelectronics-Photonics

By

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Abstract

The absorbance and photoluminescence measurement of semiconductor CdSe/ZnS core shell nanocrystals were reviewed and investigated after they were exposed to proton irradiation. The CdSe/ZnS core shell nanocrystals of 3.2nm and 4.4nm were commercially purchased and investigated. These nanocrystals were embedded in UV resin. Proton irradiation of energy 2MeV was applied at doses from $3 \times 10^{13}$ protons cm$^{-2}$ to $1.47 \times 10^{15}$ protons cm$^{-2}$ for both nanocrystal sizes. Absorbance measurements were conducted at 300K. Results from absorbance measurements showed slight broadening of the first exciton peak of both samples but was most noticeable in the 3.2nm nanocrystal sample. UV resin proton irradiation was potentially attributed to this result. Photoluminescence results were conducted at both 300K and 77K. An increase in intensity was observed at the first proton irradiation dose but then intensity degradation as the irradiation dose increased. This first increase in PL intensity was potentially due the reduction of the phonon bottleneck or displacement damage causing additional relaxation paths. Though degradation was observed in the absorbance, photoluminescence and integrated area of these spectrums, the tolerance displayed throughout the doses without totally diminishing the optical spectrums, makes CdSe/ZnS a competitive candidate for future optoelectronic material for space applications.
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Chapter 1: Introduction

Semiconductor core/shell nanocrystal devices can potentially be the answer to negative performance attributes of other semiconductor devices in space environments. They represent a candidate for a radiation tolerant alternative to commercially used photovoltaic materials. With their unique electrical and optical properties, they hopefully will cater to the demand for miniaturization of devices while ensuring that they are faster, exhibit low performance degradation under radiation and devices that are less expensive.

Advancements in the fabrication and synthesis of nanostructures and particles have ushered in a wide range of interesting materials [1]. Because of the optical and electrical properties of semiconductor nanocrystals, they possess the ability to have many useful applications. Applications such as fluorescent biological labeling [2], LEDs [3], solar cell [4], lasers [5], optical switches [6], quantum dot memories [7] make these materials very interesting materials for researchers.

1.1 Semiconductor Materials

Bulk semiconductor materials are of the macroscale, and the energy of its band gap, which is between the valance band and the conduction band, is fixed [7]. Having this characteristic, there are limits and restrictions to specific bulk semiconductors options and potential applications. In a direct gap semiconductor, an electron hole pair is created. This occurs when energy is absorbed from photons, creating an electron to be promoted from the valence band to the conduction band. The bandgap energy ($E_g$) as shown is the Figure 1.1 is:
\[ E_g = \hbar \omega \]  

where \( \omega \) is the frequency and \( \hbar \) is Planck’s constant.

In these materials, the electron has zero dimensional confinement and is able to move in all three directions [8]. The absorbance spectrum for a bulk semiconductor has a continuous spectrum until it reaches its cut off wavelength where the photon energy is not sufficient to promote an electron to the conduction band.

Quantum wells are two dimensional systems due to electrons motion restricted to \( k_x, k_y \) planes. The energy in this system is governed by the following formula:

\[ E = \hbar \left( \frac{\hbar}{2m^*} \left( k_x^2 + k_y^2 \right) + E_z \right) \]

\( k_{x,y,z} \) being the wavevectors for the three directions and \( m^* \) the effective mass.
Quantum wires are two dimensional systems leaving electron motion restricted to just one direction governed by the equation:

$$E = h \frac{\hbar}{2m} \left(k_j^2\right) + E_x^i + E_z^i$$  \hspace{1cm} (3)

1.2 Semiconductor Nanocrystals

Semiconductor nanocrystals, also known as quantum dots, have a diameter ranging from around 2-20nm. Due to its dimensions, having a radius comparable to bohr’s radius ($a_0$) it is a three dimensional systems where the electrons and holes confinement is three dimensional, creating optical and electrical properties that are very intriguing[9]. This is created due an increase in the surface to volume ratio while size of the particle decreases. When the size of the semiconductor nanocrystal becomes smaller than the materials bohr exciton radius $a_B$ which is

$$a_B = \frac{\varepsilon m^*}{m} a_0$$  \hspace{1cm} (4)

where $\varepsilon$ is the dielectric constant, $m$ is the rest mass of an electron and $m^*$ is the atomic particle, it is considered in the intermediate confinement regime. This is shown in Figure 1.2. With the exciton confined within the nanocrystals, treatment of the energy levels becomes complicated since it is too large to be treated on the molecular models but too small to be treated as a bulk material [10].
The physics of nanocrystals can be better understood by adopting the particle in a box model. This is done by modeling a quantum dot as a semiconductor in an insulating matrix. In a three dimensional potential well, photoexcited carriers will exist as shown below in Figure 1.2.

Figure 1.2 a) Cartoon image when size of the semiconductor nanocrystal is large than exciton radius b) becomes smaller than the materials bohr exciton radius $a_B$

Figure 1.3 Particle in a box model where potential well formed in any dimension of $x, y, z$ in conduction and valence bands where quantized energy levels of the excited carriers are created due to finite size of the photoexcited semiconductor nanocrystal[10]
This causes a ladder of quantized energy levels within the conduction and valence band. Because of these characteristics, semiconductor nanocrystals are also called “artificial atoms”. This is different compared to bulk semiconductor, quantum well and quantum wire energy levels [11].

It creates a size dependent energy gap governed by:

$$E_g \approx E_{g,0} + \frac{\hbar^2 \pi^2}{2m_{eh}R^2}$$

where $R$ is the radius of the nanocrystal and $m_{eh}$ which is:

$$m_{eh} = m_h m_e(m_h + m_e)$$

where $m_e$ and $m_h$ are mass of electron and hole respectively. Therefore decreasing the size of the nanocrystal will produce a blue shift in its absorbance and emission wavelengths. This also gives these particles discrete atom like energy level which is why they are sometimes called ‘artificial atoms’. Optical spectrums of nanocrystals will be enhanced because of its characteristics and properties. The photoluminescence emission intensity will be greater due to increased excitonic oscillator strength because of three dimensional confinement [13].

1.3 CdSe/ZnS

Cadmium selenide (CdSe) is of interest because it was one of the first semiconductor nanocrystals that was successfully synthesized with sufficiently high quality that the electronic structures size dependence was confidently understood. These colloidaly grown II-VI direct band gap semiconductor nanocrystals have a band energy that lies within the visible spectrum of the electromagnetic spectrum. This attribute,
added with the relatively economical cost of synthesis and high stability properties, makes it a very intriguing material for researchers [10].

CdSe has a band gap of 1.8eV at room temperature, which is 690nm in wavelength and a bohr radius of 5.6nm. Improvement of the photoluminescence quantum yield and stability can be created by growing a thick shell around the CdSe core, which possesses a wide band gap. It aids in passivating dangling bonds present on the core CdSe surface [14]. Figure 1.4 shows the CdSe/ ZnS band diagram.

![Figure 1.4 CdSe/ZnS band diagram where CB represents the conduction band and VB represents the valence band. $E_u$ and $E_h$ are the electron and hole energy [14]](image)

1.4 Synthesis Technique of Colloidal Nanocrystals

Over the years, multiple quantum dot growth methods have emerged. Molecular beam epitaxy (MBE) [15], metalorganic-chemical-vapor-deposition (MOCVD) for quantum dots [16], and vapor-liquid solid (VLS) for quantum wires [17] are some techniques. These methods require relatively expensive equipments and machinery to
produce these quantum dots. On the other hand, colloidal chemical growth is a relatively cheaper method.

Pyrolysis of precursors that are metal organic in heated solvents is one of the most efficient methods to create good quality and monodispersity of semiconductor nanocrystals [10, 18]. Dinegar and La Mer’s studies have created a commonly used method of colloidal particle nucleation and growth. In this method dimethylcadmium and trioctylphosphine selenide were the organometallic precursors and tricylphosphine oxide (TOPO), are the coordinating solvents at temperatures between 150° and 360°. The precursors were injected into the coordinating solvents and the nanocrystals were grown at temperatures between 290° and 300°C. Size-selective precipitation methods were used to collect the powdered nanocrystals using methanol. It was then dispersed in hexane and then added to solution. This 5g TOPO solution was kept under vacuum for a number of hours, was heated at 190° and cooled to 60°, where trioctylphosphine was then added [18, 19, 20, 21]. Figure 1.5 shows the growth process according to La Mer model. In this model monodisperse colloidal nanocrystals are created by having a discrete nucleation period flowed by a growth period of decreased speed by slowing the precursor addition [22].
The Zn and S precursors were Diethylzinc (ZnEt₂) and hexamethyldisilathiane (TMS)₂S. The reaction flask containing the CdSe nanocrystals was heated under N₂ and the Zn and S precursors were added at temperature ranging from 140° to 220°, and were vigorously stirred over a period of 5-10 minutes. After the mixture was cooled to 90° and left stirring for several hours, they were then recovered as powder by precipitation using methanol [18, 23].

The temperature at which the shell precursors were added was very critical, because if the temperature was too high the core CdSe would have increase in size due to Ostwald ripening. This would increase the non-uniformity of nanocrystal size and therefore broaden the spectral line widths. If the temperature was too low, the shell
crystallinity would be decreased due to incomplete decomposition of the precursors. The rate at which the precursor was added as well as the concentration of the ZnS precursor was also critical. Slowly adding the precursor at low concentrations enhanced the homogeneous distribution of the ZnS shell onto the CdSe core nanocrystals [18].

1.5 Core/Shell Nanocrystals

Size dependability in semiconductor nanocrystals is very important. The quantum confinement effects that the nanocrystals possess are directly related to the dimensions of the particles. This size dependent quantum confinement property is directly related to absorption and emission of the nanocrystals. Because of semiconductor nanocrystal’s tune-ability of the band gap, it is essential that these nanocrystals are highly stable. In order to take full advantage of these nanocrystal’s unique and desirable properties, certain properties have to be optimized such as stability against degradation and high crystallinity. Due to Oswald ripening, nanocrystals tend to aggregate together forming large clusters because of their high surface tension [24, 25].

To counter this, the core CdSe nanocrystals can be coated with a higher bandgap inorganic material ZnS shell. This allows chemical and electronic passivation of surface dangling bonds which increases photoluminescence quantum yield. It also creates room temperature photostability due to passivating nonradiative recombination. Unwanted agglomeration, growth and oxidation are blocked and the particle become more robust, increasing its tolerance to process conditions for optoelectronic devices. It also introduces the ability of the nanocrystal’s surface to be modified. With this feature nanocrystals can be disperse and can become soluble in various substances [24, 26].
1.6 Radiation in Space

Radiation is essentially energy traveling in the form of waves. There are two types of radiation, ionizing and non ionizing. Non ionizing radiation is not a threat because it does not have sufficient energy to ionize another material while ionizing radiation does. The radiation from various objects travel from extremely far distances, so it is important to note that the radiation that is observed from planets and stars can be a result of an event that happened millions of years ago. Some sources of radiation in space are pulsars, black holes, hot stars, cold stars planets and interstellar dusts, interstellar molecules and quasars, and galaxies [27].

1.6.1 Magnetosphere

To understand radiation in space you must first understand the space environment. Earth would have a dipole geomagnetic field, but due to solar winds from the sun the shape of these magnetic field lines is altered. The solar wind is a flow of plasma from the sun [28]. The earth’s magnetosphere is shown in Figure 1.6.

![Figure 1.6 Earth’s magnetosphere and how the geomagnetic field lines are altered due to the solar winds][29]
The magnetic fields trap charged particles into the Van Allen belts, which are shown above as the inner and outer zone. Because of the magnetic field geometry, the South Atlantic Anomaly (SAA) region is created where the radiation belts are at their lowest. The SAA has a high proton flux and is in a localized region having a fixed altitude within the inner radiation belt [30].

1.6.2 Ionizing Radiation Sources

The ionizing radiation sources in space are protons trapped in the Van Allen radiation belts, galactic cosmic rays and solar particle events [31].

Galactic Cosmic rays

Galactic cosmic rays represent the predominant radiation outside of the magnetosphere. Protons are responsible for approximately 87% of cosmic rays. Helium ions make up 12% and 1% is High-Z and High-Energy particles [31].

Cosmic rays are constantly hitting the surface of the earth. They may not be felt on earth due to the terrestrial atmosphere shielding the majority of the radiation, but it is a definite factor in outer space. When cosmic rays of high energy strike atoms and molecules in outer space they create showers of subatomic particles that constitute secondary cosmic radiation that is an additional factor in space [27].

Primary cosmic radiation consists of or includes dust and gas that is gradually accelerated due to magnetic fields that act like gigantic accelerators from outside the solar system. These charged particles such as electrons, neutrons and protons spread over a range of energies. This will cause the performance of semiconductor devices to be severely damaged [14, 32]. Potential sources of cosmic radiation are pulsars, supernova
explosions and the shock wave acceleration of matter in the interstellar medium. The energy of these galactic cosmic rays can be as high as $10^{11}$ eV [27, 29].

**Solar Particle Events**

There are two types of solar particle events, which are solar flares and coronal Mass Ejection (CME). Solar particle events can be damaging to missions around the poles, on geosynchronous orbits and in free space. Solar flares are large emissions from the sun containing protons, helium and heavy ions [29, 31].

Occasional intense radiation from the sun is also known as solar flares. When localized storage energy in the coronal magnetic fields becomes too great, there is a burst of energy released. Solar flares maximum energy is higher than 0.1GeV but are typically lower. They consist mainly of electrons and last for hours [29].

Coronal Mass Ejection (CME) is a large plasma eruption that accelerates particles. It comprises of mainly protons and lasts for days. The Protons are sometimes of magnitude higher than primary cosmic rays and though harmless to earth can me a major issue for devices in space [27, 29].

**Trapped Particles in the Radiation Belts**

The magnetosphere acts as a cavity protecting the earth from radiation. A significant weakness in this cavity is the poles, where the geomagnetic field lines are somewhat vertical. This allows particles a possibility to penetrate the upper atmosphere. These particles then become trapped inside by the magnetic field and form the Van Allen radiation belts. Figure 1.7 shows how the trapped particles within the Van Allen radiation belts travel along the magnetic field lines.
The particles undergo three types of motion: gyration, drift and bounce. They gyrate around the field lines, they bounce from one end of the field line to the other and they drift around the world in longitude [34]. The radiation belts have a toroidal shape and have an upper and lower limit. The lower limit of the radiation belt is the earth’s atmosphere and the upper limit is defined by the minimum intensity of the electric field in order to keep the particles trapped. The particles within the radiation belts are mainly proton 1keV to 300MeV and electrons 1keV to 10MeV [29].

1.7 Radiation of Semiconductors

The study of radiation effects in semiconductors and finding materials of greater tolerance to the radiation in space environments is very important. The importance and value of electronic devices in space is rapidly increasing due to increased explorations to other planets and actual research in outer space environments. Scientist heavily depend on the durability and functionality of these semiconductor electronic devices as the duration of these explorations are prolonged. Also, photovoltaic devices are heavily used
in space, utilizing solar energy, so the study of radiation affects in space is definitely an important topic [32, 35].

Radiation bombardment on semiconductor devices causes harmful defects. Divacancies and displacement are formed in silicon lattice atoms due to radiation damage. In semiconductors, like impurity atoms, defects can introduce local energy states into the band structure. In certain semiconductors with specific lattice electronic characteristics, defects may act as donors seizing holes in p-type or yielding electrons thermally excited in n-type, may act as acceptors thermally ionizing to produce hole in p-type or seize electrons in n-type, or they may act as amphoteric centers capturing holes in p-type and electrons in n-type [35].

Defects introduced by irradiation in semiconductors alter its electronic behavior. The carrier concentrations of semiconductors can be altered to the point of inducing conversion from p-type to n-type and vice versa. Charge centers introduce carrier scattering and influence non equilibrium minority carrier processes like trapping and recombination by deep level defects. These act as efficient traps and recombination centers [35].

Protons cause displacement and ionization damage to semiconductor devices causing tremendous threat to orbiting spacecrafts and electronic devices. The size of the proton causes extreme displacement damage in the semiconductor lattice. It is the primary reason why semiconductor devices undergo failure and performance degradation [32].

Quantum dots have an advantage over bulk semiconductor devices for semiconductor optoelectronic device application due to their dimensions. Due to
nanocrystals exciton undergoing three dimensional confinement, the probability of carrier nonradiative recombinations caused by radiation induced defects, will be reduced [32].

1.8 Spacecrafts in Space

For spacecrafts travelling through these harsh radiation environments, there are many things to consider. There is a vast variation in the amount of radiation flux that a spacecraft will encounter while on its orbit depending on the trajectory through the different radiation sources. The low earth orbits (LEOs) travel through proton and electron particles due to them being trapped in the Van Allen belts. The flux levels through this orbit, depends greatly on the orbits inclination angle and altitude [31, 33].

In this orbit the inclinations affect on the flux are most dependant between 0 - 30°. The above this inclination the flux rises gradually until above 60° where the inclination has little affect on the flux levels. The inclination is important at LEOs because they tranverse through the SAA and the north and south poles are less shields by the geomagnetic fields making them high flux values at other LEOs[31].

For the altitude, the flux levels encounter the greatest increases between the ranges at altitudes 200 – 600km, where above this flux increase is more gradual. Though as the altitude increases there will be a gradual increase in the flux, the inclination affects on the flux in more important because as the inclination increases, the time spent by devices in these hazardous zones are increased.

Highly elliptical orbits (HEOs) pass through the Van Allen belts like the LEO orbits but because of their high altitudes of greater than 30,000km they experience long
exposures to solar flares and cosmic rays regardless of inclinations. Geostationary orbits (GEOs) are nearly fully exposed to proton fluxes from solar flares and cosmic rays.

Over the years the power requirements for satellites have steadily increased. Space power generation requires higher efficiency and radiation tolerance in the future due to satellite systems need to fly in an orbit of 2000 to 10000 km altitude which is the medium earth orbit (MEO). Even with protective coverglass, crystalline solar cells still experience performance degradation.

A device in space, even if shielding is employed from protons and electrons, particles that transverse a point in the actual device will possess ranges of energies from a few eV to 100 MeV. Up to 10-15% over 50 years in the geostationary orbit and 50% in orbits of high proton irradiation fluxes [36, 37, 38].

1.9 Overview of Thesis

This thesis will show that semiconductor CdSe/ZnS nanocrystals are a valid candidate for semiconductor materials for space application. This is proved by showing that they have a high tolerance for proton irradiation, which is the main radiation source in space which negatively affects the performance of semiconductor materials in space. It will show that the absorbance spectrum and photoluminescence results of these CdSe/ZnS materials prove that the optical properties of the materials are not diminished through the range of radiation doses investigated in this thesis.
Chapter 2: Instrumentation and Experimental Procedure

Due to the stability and low cost of colloidally synthesized II-VI semiconductor nanocrystals, they are of much interest. Because of the bandgap being located within the visible spectrum, they have gained major interest in solar cell device fabrication for space application. An issue that has been revealed with these nanocrystals is finding an adequate polymer medium, such as a conductive polymer, to matrix them in, while assisting in the carrier transport for solar cell application. Also, solar cell devices in space will have to endure and tolerate radiation from the space environment.

To analyze the how the optical properties of the CdSe/ZnS Core/Shell semiconductor nanocrystals are affected by proton irradiation induced defects and degradation, CdSe/ZnS Core/Shell nanocrystals embedded in an ultra violet (UV) resin, were commercially purchased from Evident Technologies.

2.1 Ultra Violet Curing of Resin

The resin used to matrix the nanocrystals in was a polyurethane oligomer mixture. The nanocrystals used in this thesis were of diameter 4.4nm and 3.2nm with size measurements provided by the manufacturer using tunneling electron microscopy. Two 4.4nm and 3.2nm CdSe/ZnS nanocrystal samples were prepared by evenly drop-casted onto c-plane sapphire wafers. Each sample was then cured under a 200 W UV power source for 90 minutes.
2.2 Absorbance

When light is incident on a medium it can be reflected, propagated through the medium, or it can be absorbed. Absorption occurs when the frequency of light incident onto a medium is resonant with the frequency of the atoms of the medium. Quantification of light being absorbed by a medium is measured by the absorption coefficient \( \alpha \). This is used in Beer’s law which is

\[
I(l) = I_0 e^{-\alpha l}
\]  
(6)

where \( I(l) \) is the propagated light through a medium in the \( l \) direction, \( I_0 \) is the optical density when \( l = 0 \).

Absorption can also be quantified as optical density (O.D.) and is sometimes called absorbance \( (A) \) which is

\[
\text{O.D.} = A = -\log_{10}(\frac{I(l)}{I_0})
\]  
(7)

where \( l \) is the medium’s length. Therefore the absorption coefficient can be determined as

\[
\alpha = \frac{(\text{O.D.})}{l \log e} = \frac{2.303(\text{O.D.})}{l}
\]  
(8)

From the optical density other optical magnitudes can be derived such as transmittance \( (T) \) and absorbance \( (A) \). Transmittance and absorbance can also be expressed as

\[
T = \frac{l}{I_0}
\]  
(9)

\[
A = 1 - \frac{l}{I_0}
\]  
(10)

[39, 40].
Due to quantum confinement, the band gap of the semiconductor nanocrystals can be altered by varying the diameter of the nanocrystals. This is shown in Figure 2.1. The absorbance measurements were normalized to for easier interpretation.

Fig. 2.1 Size dependence of excitonic peak in CdSe nanocrystals
2.3 Absorbance Measurements

Absorbance measurements were carried out using the Varian Cary 500 UV-VIS Spectrophotometer. The Varian Cary 500 UV-VIS Spectrophotometer could run absorbance spectra from 175-3300nm. It used a PbS detector that was thermoelectrically cooled to 0° to reduce photometric noise.

Absorbance measurements of the sample’s first exciton peak were collected for each sample scanned from wavelengths from 1000nm to 200nm. After samples were irradiated, the absorbance measurements were again measured. Irradiation doses ranged from $3 \times 10^{13}$ protons cm$^{-2}$ to $1.47 \times 10^{15}$ protons cm$^{-2}$ at irradiation energy of 2MeV. This process was carried out for all proton irradiation doses. The integrated area of the absorbance was then analyzed and compared across all the doses.

2.4 Photoluminescence

Luminescence is somewhat the opposite of absorption. In a two level atomic system, when the electrons, after being excited to the conduction band, return to its ground state, photons are emitted. This de-excitation process is luminescence. Photoluminescence is luminescence occurring from photon excitation. Figure 2.2 gives an overview of interband photoluminescence in a direct band gap semiconductor.
Energy from the photons incident on a material are absorbed by the material, promoting electrons from the valence band into the conduction band. This energy, $\hbar\omega_L$, is greater than the band gap energy $E_g$ and therefore greater than the radiated photon emission energy $h\omega$. The electrons then rapidly relax to the lowest level in the conduction band of $\sim k_B T$ to the bottom of the excited energy level where $k_B$ is Boltzmann’s constant and $T$ is temperature in Kelvin [39].

Radiative emission of photons is not the only way that electrons from the conduction band can be demoted to the valence band. Nonradiative emission is also a
method for the electrons from the conduction band to drop down to the ground state energy. In this method electrons may lose excitation energy via loss of heat as phonon emission or it may transfer energy to defects or impurities which act as traps. This causes electrons in the conduction band to settle in the bottom of the conduction band and holes in the valence band to accumulate at the top of the valence band [40].

Due to nonradiative recombination during the photoluminescence process, the energy of the photons absorbed tends to be greater than the energy of the emitted photons.

This phenomenon is called stokes shift and is the energy difference between the photon absorption energy $\hbar \omega_L$ and the photon emission energy $\hbar \omega$. In Figure 2.3, the CdSe/ZnS samples go from having an absorbance wavelength of 600nm to having a photoluminescence wavelength of 629nm, which a loss of energy due to the energy formula

$$E = \frac{hc}{\lambda}$$

(12)

2.5 Photoluminescence Measurements

In normal photoluminescence spectra measurements there are two types of spectra, emission spectra and excitation spectra. The emission spectra are done by excitation wavelength and the emitted light intensities are detected and recorded at different wavelengths. In excitation spectra measurements, the emission wavelengths are fixed and the excitation wavelengths are scanned through a range [39].

Photoluminescence measurements were measured using the Bomem Fourier Transform Infrared (FTIR) spectrophotometer. Photoluminescence measurements were
made for all samples after each proton irradiation dosage at temperatures 77K and 300K which varied ± 1K using liquid nitrogen.

2.6 Proton Irradiation Measurements

The irradiation of the samples took place at the Naval Research Laboratory (NRL) in Washington DC. The samples were wrapped in lint free tissue and placed in sample holders before being sent for irradiation. A Van De Graaff accelerator was used to irradiate the samples.

The doses listed in Table 1 in Chapter 3 are the actual doses received by each sample at NRL. The accumulated dose was used for analysis of the data
Chapter 3: Results

Table 3.1 shows the irradiation of each sample at 2MeV.

<table>
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<tr>
<th>Sample</th>
<th>Dose 1 (protons cm(^{-2}))</th>
<th>Dose 2 (protons cm(^{-2}))</th>
<th>Dose 3 (protons cm(^{-2}))</th>
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<td>4.00 x 10(^{14})</td>
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<td>3.00 x 10(^{13})</td>
<td>1.55 x 10(^{14})</td>
<td>7.00 x 10(^{14})</td>
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<td>4.4nm NC s2</td>
<td>5.00 x 10(^{13})</td>
<td>4.00 x 10(^{14})</td>
<td>1.47 x 10(^{15})</td>
</tr>
</tbody>
</table>

Table 3.1 Irradiation table showing fluence on each sample

3.1 Absorbance Results

All absorbance results were measured using the Cary 500 spectrophotometer at 300K. Figure 3.1 shows the absorbance spectra of the 3.2nm NC S1. The absorbance spectrum for each dose was vertically scaled to more effectively compare the results of each sample. As the proton irradiation dose increased, a slight broadening of the exciton peak was observed. This was expected if degradation increased with an increase in proton irradiation dose or fluence.
The same procedure of absorbance analysis was used for each sample in Figures 3.2, 3.3 and 3.4.
Figure 3.3 Absorbance Spectrum for all doses of 4.4nm NCs S1

Figure 3.4 Absorbance spectrum for all doses of 4.4nm NCs S2
The absorbance spectrum was further investigated by analyzing the integrated area of the absorbance spectrums for each proton irradiation dose. This was calculated using the grams software which measured the integrated area from the two end points of the peak as shown in Figure 3.5 and the results are shown in Figure 3.6.

Figure 3.5 illustration of how integrated area is measured

Figure 3.6. Integrated area of absorbance spectrum for all doses of all samples
Analyzing the integrated area results, the 4.4nm samples were less affected by the proton irradiation when compared to the 3.2nm samples. The 4.4nm samples integrated area at the last dose nearly approached the initial values. In comparison the 3.2nm samples integrated area shows a reduction to as much as half its original integrated area.
3.2 Photoluminescence Results

To excite the samples for the photoluminescence measurements a 65mW green laser was used. All settings during the PL measurements were consistent for all samples. The helium neon alignment laser located at 632nm was present in the spectrum but its influence was subtracted from all calculated data. The PL measurements were recorded for all doses are shown in Figure 3.7 and 3.8 at 300K and 77K.

![Figure 3.7 PL spectrum for all doses of 3.2nm NCs S1 at 300K](image_url)
In the PL results of Figure 3.6 and 3.7, a reduction of the PL intensity was observed as the proton irradiation dose was increased. Also, increased PL intensity was observed at the first dose application on the 3.2nm NCs S1. This will be discussed later in the discussion chapter as an increase in the phonon bottleneck at low doses. Similar phenomenon was observed in other samples and shown below in their PL results in Figures 3.9-3.14.
Figure 3.9 PL spectrum for all doses of 3.2nm NCs S2 at 300K

Figure 3.10 PL spectrum for all doses of 3.2nm NCs S2 at 300K
Figure 3.11 PL spectrum for all doses of 4.4nm NCs S1 at 300K

Figure 3.12 PL spectrum for all doses of 4.4nm NCs S1 at 77K
Figure 3.13 PL for all doses of 4.4nm NCs S2 at 300K

Figure 3.14 PL for all doses of 4.4nm NCs S2 at 77K
The PL results of the 4.4nm NCs S2 at 77K was the only result that did not show the increase in PL intensity at low dose. All samples showed a decrease in PL intensity as the proton irradiation dose increased. The variation in the PL intensity peak wavelength was displacement of lattice atoms by the proton bombardment, creating defects within the bandgap.

3.2.1 Integrated Area

The integrated area of the PL measurements was also analyzed. The helium neon laser’s influence in the integrated area was subtracted to obtain these results. This was done for all proton irradiation doses on each sample and shown in Figures 3.15 and 3.16.

![Graph showing integrated area of PL for all doses at 300K](image)

Figure 3.15 Integrated area of PL for all doses at 300K
The integrated area results showed a reduction in the integrated area for increased proton irradiation dose, but also showed what was reflected in the PL results, which was an increase in the integrated area at low fluence for all but one, which will be explained in the next chapter.

3.2.2 Full Width at Half Maximum (FWHM)

The FWHM of the PL measurements was also measured. This analysis was done for all samples for both 300K and 77K measurements and shown in Figures 3.17 and 3.18.
Figure 3.17 FWHM of PL for all doses at 300K

Figure 3.18 FWHM of PL for all doses at 77K
For the 300K results, an increase in FWHM of up to 12% was observed throughout increases in fluence. At 77K, an increase in the FWHM of up to 21% is observed in these results which will be discussed in the Chapter 4.
Chapter 4: Discussion of Results

The results confirmed that semiconductor core shell nanocrystals tolerated the proton irradiation doses which were up to $1.47 \times 10^{15}$ protons cm$^{-2}$ at 2MeV without diminishing their optical spectrums by more than 25%. The CdSe/ZnS nanocrystals have a band gap which lies within the visible range which makes it a potential candidate for solar cell applications. Semiconductors exposed to proton irradiation cause structural defects and displacement damage which result in device performance degradation and failure. Localization of the exciton in a nanocrystal due to three dimensional confinement reduces the occurrence of nonradiative recombination and defect that are located in the lattice structure. This high tolerance to proton irradiation makes it a valid candidate for electronic application in space [41].

In the results above the absorbance measurements were first analyzed. The 3.2nm nanocrystals showed a slight broadening of the first exciton absorbance peak as the fluence of the proton irradiation increased. The absorbance spectrum of the 4.5nm CdSe ZnS nanocrystals are also displayed and analyzed. The absorbance results of these displayed even less of a broadening of the first exciton absorbance peak. This broadening was attributed to the radiation tolerance of the UV resin in which the CdSe/ZnS nanocrystals were embedded in [14].

The integrated area results from the absorbance results showed that with increasing the proton irradiation doses the integrated area was only slightly reduced for both 3.2nm and 4.5nm CdSe/ZnS nanocrystals. This demonstrated that these nanocrystals withstood proton irradiation throughout the doses of $3 \times 10^{13}$ protons cm$^{-2}$ to $1.47 \times 10^{15}$ protons cm$^{-2}$. 
Photoluminescence measurements were done at 300K and 77K. For both 3.2nm and 4.5nm CdSe ZnS nanocrystals PL results, the PL intensity demonstrated a slight increase in intensity at low doses.

The photoluminescence increase at low doses was attributed to the nanocrystals three dimensional confinement properties. The phonon bottleneck reduction by defect assisted phonon emission was an explanation. When the electrons from the phonon’s within the conduction band undergo decoupling, which occurs when level splitting is greater than the phonon energy, single phonon emission energy relaxation is suppressed. This phenomenon is due to energy and momentum requirement and is called the phonon bottleneck [41, 42]. Displacement damage may have caused deep level defects which created additional relaxation paths for thermalization carriers [32].

Shifts in the photoluminescence peak were observed as the dose increased. This was due to displacement of lattice atoms of the nanocrystals creating defects within the bandgap.

This phenomenon was also reflected in the integrated area of the PL measurement. After the first dosage all samples did show a decrease in integrated area but these samples still withstood the proton irradiation all the irradiation doses without totally diminishing their optical spectrums. This decrease was attributed to nonradiative recombination and defects within the nanocrystal induced by the proton irradiation. Both 3.2nm and 4.4nm samples are functional throughout all doses.

The full width half maximum (FWHM) results show that the irradiation of the nanocrystals resulted in up to a 12% and 21% increase of FWHM at 300 and 7K respectfully. This was caused by lattice structural displacements and defects inducing
nonradiative recombination. Also, proton radiation caused non uniformity of the nanocrystals causing broadening the photoluminescence and therefore altering FWHM [32].

Comparing the CdSe/ZnS nanocrystals proton irradiation tolerance GaAs quantum well structures proves that they are more tolerant. GaAs/AlGaAs quantum well semiconductor materials exhibit and observe intersubband transitions up to proton irradiation 1MeV with doses of 5.0 x 10^{14} \text{cm}^{-2}[43]. This is shown in Figure 4.1 and 4.2.

**Figure 4.1** GaAs/AlGaAs quantum well absorbance spectrum at 77K [43]

**Figure 4.2** Absorbance spectra of GaAs/(AlGaAs-GaAs) multiple quantum wells at 77K [43].
In this material the degradation of absorbance was due to the proton irradiation inducing defects. The defects which were created trap the two dimensional electrons in the quantum wells. Figure 4.1 shows the increased degradation of these quantum well structures as the irradiation dose reached $6 \times 10^{13}$ protons cm$^{-2}$.

Figure 4.2 also shows the absorbance spectra of quantum well structures as irradiation dose increases. This figure illustrates that at $3 \times 10^{13}$ protons cm$^{-2}$ the absorbance signal was almost completely diminished, which compared to the results in this thesis was less that the first dose applied to the nanocrystal samples. Even though Figure 4.1 and 4.2 absorbance measurements were conducted at 77K, whereas in this thesis absorbance measurements were conducted at 300K, comparison is possible. The temperature dependence of CdSe/ZnS nanocrystals band gap $E_g(T)$ is governed by:

$$E_g(T) = E_g(0) - \alpha T^2/(T + \Theta_D),$$

(13)

where $E_g(0)$ is the bandgap at 0K, $\alpha$ is a constant and $\Theta_D$ is the 0K Debye temperature [44]. For the purposes of analysis, absorbance degradation can still be compared because what was analyzed was the degradation of the absorbance peak and not the shift in the bandgap.

Further analysis on quantum well structures has taken place. Photoluminescence emission of InGaAs quantum well (QW) structures alongside quantum dots (QD) have been studied through various proton irradiation doses.
Figure 4.3 shows that the PL peak intensity of various quantum dots and InGaAs QW’s. The PL measurements were tested at 80K and proton irradiation doses range from $1.3 \times 10^{11}$ to $3.5 \times 10^{13}$ protons/cm$^2$ at 1.5MeV. The Peak PL intensity of the QW is $\sim 30$ times lower than when non-irradiated. Figure 4.3 also shows that the quantum dot structures have a high tolerance to the proton irradiation [41].

In quantum wells, the carriers are mobile and carriers moving along the well plane will find defects induced by proton irradiation. In semiconductor nanocrystals, because of their three-dimensional confinement carriers can only undergo nonradiative combination when the defect is present within with nanocrystal, making these nanocrystals more proton irradiation tolerant compared to quantum well and other quantum materials [43].
Bulk devices, such as GaAs LED devices, suffer from damage at as low as $1 \times 10^{10}$ protons cm$^{-2}$ [43]. Quantum well based devices have a greater tolerance to proton irradiation compared to bulk semiconductors [45]. Quantum dots and nanocrystals having an even greater tolerance to proton irradiation compared to quantum wells, makes them an even more valuable candidate for space application [32, 41, 46].
Chapter 5: Conclusion

The work has shown that CdSe/ZnS semiconductor core/shell nanocrystals are significantly more tolerant to proton irradiation than bulk semiconductor and other quantum materials. It is a definite candidate for an alternate solar cell material for space application.

Bulk semiconductor materials and present solar cell devices succumb to tremendous damage due to the radiation in space [35]. Polycrystalline thin film semiconductor materials are commonly used due to their low cost, relatively good efficiency and stability but for space application, they are not tolerant to the harsh space environments.

CdSe/ZnS core shell nanocrystals embedded in an ultraviolet resin were commercially purchased from Evident Technologies. These II-VI semiconductor nanocrystals have a bandgap that lie within the visible wavelength range. This property allows for these materials to possess a bandgap throughout the visible wavelength spectrum simply by varying the size of the nanocrystal.

Samples were sent for proton irradiation at the Naval Research Laboratory lab in Washington D.C. Two samples of nanocrystal core diameter 3.2nm and 4.4nm each were fabricated and tested. Proton irradiation of energy 2MeV and doses from $3 \times 10^{13}$ to $1.47 \times 10^{15}$ protons cm$^{-2}$ were deposited.

Absorbance measurements were conducted on the samples using the Cary 500 spectrophotometer. Absorbance results concluded that the CdSe/ZnS nanocrystals possessed exciton peaks within the visible spectrum. The samples displayed tolerance throughout the radiation doses with slight broadening of the exciton peak as the
irradiation dose increased. The smaller diameter nanocrystals displayed more visible broadening of the exciton peak.

Photoluminescence measurements were carried out using the Bomem DA8 spectrometer. The results indicated that as the irradiation doses increased, there was a decrease in PL intensity and integrated area. At low doses, there was an increase in PL intensity and integrated area which was attributed to the reduction of the phonon bottleneck as well as to displacement damage that may have caused deep level defects which created additional relaxation paths for thermalization carriers.

Unfortunately, this experiment’s samples were lost at the NRL when sent for a further irradiation cycle. With further doses, more information may be understood about the nanocrystals radiation tolerance and also the UV resin’s tolerance. The damage done to the UV resin hinders in investigation on nanocrystals optical properties after irradiated at certain doses, and is the probable explanation for the broadening of the absorbance exciton peak of the smaller nanocrystal [14]. Finding innovative ways to only irradiating the nanocrystals would be beneficially in this area of research.

In terms of device fabrication, one of the hurdles that II-VI semiconductor nanocrystals like CdSe/ZnS face is that there is difficulty finding an appropriate material such as a polymer to be matrixed in, to fabricate an effective solar cell device that carrier transport is successful [14].

In all, this thesis further advanced the understanding of colloidal nanocrystals interaction with proton irradiation. Proton radiation in harsh space environments inducing defects and degradation in device performance is important because of the important space activities that are carried out by spacecrafts and satellites in these
environments. The tolerance that CdSe/ZnS displayed relative to other semiconductor materials places nanocrystals as a key component to more efficient optoelectronic devices for space application
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GaAs Quantum Well Light emitting Diodes”, IEEE Transactions on Nuclear Science,
Oh no!!! The Superhero Solar Man has some serious problems. His arch rival and once best friend has found his weakness and needs a solution immediately. His enemy Space flamer has learned about Solar mans intolerance to high energy proton radiation. Solar Man uses bulk silicon as his material to generate his energy that powers his armor. His armor consists of two rocket launchers on each arm and rocket propellers on his shoes which make him fly.

Luckily for Solar Man there is a potential solution to his solar cells intolerance to proton irradiation. Semiconductor core shell nanocrystals can be used as a substitute for bulk semiconductor materials as a solar cell material. CdSe/ZnS semiconductor nanocrystals have a bandgap which can be tuned based on the size of the nanocrystals as shown in Figure 1.

This band gap can be tuned to lay within the visible light spectrum making it ideal for solar cell application. Most importantly these CdSe/ZnS core/shell nanocrystals have been proven to have a high tolerance to proton irradiation making it perfect for Solar Man. A researcher at the University of Arkansas named Stephen Charter and his mentor, Dr. Omar Manasreh, have shown this in their research. He irradiated CdSe/ZnS nanocrystals of sizes 3.2 and 4.4nm. They displayed very high tolerances to the proton irradiation.
compared to bulk semiconductor materials. This can be seen in some of his results in Figure 2.

Figure 2. Integrated area of CdSe/ZnS nanocrystals as proton irradiation fluence increase

Figure 2 shows the integrated area of the CdSe/ZnS nanocrystals photoluminescence peaks. The results show that throughout the fluences used in their research the nanocrystals displayed a higher tolerance to the proton irradiation than bulk semiconductors, which have experience device failure at doses as low as $1 \times 10^{10}$ protons cm$^{-2}$ such as GaAs LED devices.

This is great news for Solar man because now he can fight Space flamer in space environments with high proton irradiation levels and will help him defeat his enemy Space Flamer. Thank you Stephen Charter and thank you Solar man for always saving us from Space Flamer.
Appendix B: Executive Summary of Newly created Intellectual Property

The following list of new intellectual property items were created in the course of this research project and should be considered from both a patent and commercialization perspective.

1. A method of characterizing CdSe/ZnS semiconductor nanocrystal’s proton irradiation tolerance by analyzing proton irradiation affects on absorbance and photoluminescence measurement results. The method has been used before by my former research group member Kaushik Narsingi.

2. Core/shell semiconductor nanocrystals optical characteristic relationship with proton irradiation of energy 2MeV at $3 \times 10^{13}$ protons cm$^{-2}$ to $1.47 \times 10^{15}$ protons cm$^{-2}$. 
Appendix C: Potential Patent and commercialization aspects of each numbered items in the Executive Summary

C1. The item listed were considered first from the perspective of whether or not the item could be patented.

1. The method used to characterize the proton irradiation tolerance properties of CdSe/ZnS can be patented because it characterization of materials using optical techniques is commonly used for various research topics. These methods can be very informative giving to the properties of materials.

2. The relationship between core/shell semiconductor nanocrystals and their proton irradiation properties cannot be patented. Further research must be done to further understand this relationship thoroughly. Higher doses must be applied to further analyze and understand why the optical properties are degraded.

C2. Commercialization possibility of IP

1. This method should not be patented because other researches should be allowed to further analyze CdSe/ZnS using this method and others to understand more about the proton irradiation influence. It would not be beneficial to society is these methods were patented in any way.

2. The relationship between the core/shell nanocrystals and their proton irradiation properties should not be patented because more
has to be understood about the materials interaction with these high energy protons.

C3. Possible Prior disclosure of IP

1. The method used to characterize the proton irradiation affects on the optical properties of CdSe/ZnS nanocrystals has been discussed by Kaushik Narsingi while previously in my research group from January 2006 to May 2008.

2. The relationship between core/shell semiconductor nanocrystals and their proton irradiation properties has also been discussed by Kaushik Narsingi.
Appendix D: Broader Impact of Research

D.1 Applicability of Research Methods to Other Problems

The research methods used in this thesis is applicable to many other problems. It is most applicable to alternate photovoltaic materials. The methods used in this thesis to analyze proton irradiation effects on CdSe/ZnS semiconductor materials were optical absorbance and photoluminescence. These optical measurement techniques will determine if the material is ideal for solar application, depending on whether the band gap energy lies within the visible electromagnetic wave energies range.

D.2 Impact of Research Results on U.S. and Global Society

The research results will affect the U.S and global society positively. Advances in proton irradiation tolerance of electronic devices in space will assist any type mission in space environments. Satellites in space are central component to communication, transmission of various signals with information and surveillance in the world. This makes it a matter of importance that affects the whole world. These devices in space are of great importance and proper functionality is a must. Not only will it cost millions to repair solar and other optoelectronic devices but also could be a matter of life and death depending of the responsibility of the device.

D.3 Impact of Research Results on the Environment

The research results impact the environment positively because CdSe/ZnS nanocrystals possess a band gap that can lies within the visible range. This means they are a great candidate for solar cell application. Alternative energy is an area of
tremendous attention because of oil prices and pollution’s negative effect on the earth’s environment.
### Appendix E: Microsoft Project

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Appendix F: Identification of All Software Used in Research and Thesis/Dissertation Generation

Computer #1:
   Model Number: Dell Dimension 5150
   Serial Number: DQHFX81
   Location: ELEG 3121
   Owner: Dr. Omar Manasreh

Software #1:
   Name: Microsoft Office 2007
   Purchased by: Dr. Omar Manasreh

Software #2:
   Name: Origin 7.0
   Purchased by: Dr. Omar Manasreh

Computer #2:
   Model Number: Gateway M-Series Laptop
   Serial Number: T4A8191006835
   Location: Personal Laptop
   Owner: Stephen Charter

Software #1:
   Name: Microsoft Office 2007
   Purchased by: Stephen Charter

Software #2:
   Name: Origin 8E
   Purchased by: University of Arkansas

Computer #3:
   Model Number: Dell Optiplex 745
   Serial Number: HZ221F1
   Location: ELEG 3142
   Owner: Dr. Omar Manasreh

Software #1:
   Name: Varian UV Scan Application
   Purchased by: Dr. Omar Manasreh

Computer #4:
   Model Number: Dell Optiplex GX 270
   Serial Number: 2KZ3Q51
   Location: ELEG 3142
   Owner: Dr. Omar Manasreh

Software #1:
   Name: Bomem PCDA
   Purchased by: Dr. Omar Manasreh
Software #2:
Name: Grams/32 AI
Purchased by: Dr. Omar Manasreh

___________________________   ___________________________
Stephen Charter     Dr. Omar Manasreh